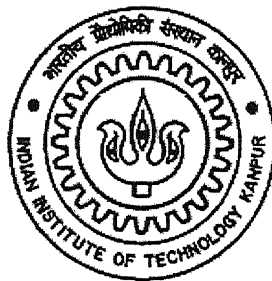


# **POLYMERIZATION OF $\epsilon$ -CAPROLACTAM UNDER NEAR- INDUSTRIAL CONDITIONS**

A Thesis Submitted  
in Partial Fulfillment of the Requirements  
for the Degree of  
**Master of Technology**

by

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## CERTIFICATE

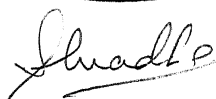
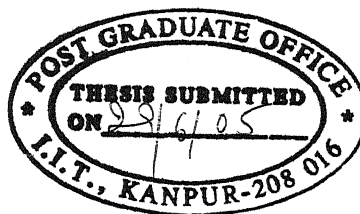
This is to certify that the work contained in the thesis entitled "**Polymerization of  $\epsilon$ -Caprolactam under Near-Industrial Conditions**", by Ramteke Manojkumar Charandas, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.



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## NOMENCLATURE

|               |  |
|---------------|--|
| $a$           | Specific interfacial area ( $\text{m}^2 \text{m}^{-3}$ )   |
| $A$           | Jacket area ( $\text{m}^2$ )   |
| $A_i$         | Frequency factor for $i$ th reaction rate constants ( $\text{kg mol}^{-1} \text{h}^{-1}$ )       |
| $c, C_s^i$    | Concentration of polymer in solution ( $\text{kg}/100 \text{ kg}, \text{g cm}^{-3}$ )            |
| $[C_i]$       | Concentration of caprolactam (1) and cyclic dimer (2) in liquid phase ( $\text{mol/kg}$ mixture) |
| $C_{p,i}^v$   | Specific heat of pure $i$ in vapor phase ( $\text{kJ kg}^{-1} \text{K}^{-1}$ )                   |
| $C_{p,mix}^l$ | Specific heat of liquid reaction mixture ( $\text{kJ kg}^{-1} \text{K}^{-1}$ )                   |
| $d_s$         | Diameter of stirrer (m)  |
| $D_i$         | Diffusivity of component $i$ ( $\text{m}^2 \text{h}^{-1}$ )                                      |
| $D_r$         | Diameter of reactor (m)  |
| $D_w$         | Reactor wall thickness (m)   |
| $DP$          | Degree of polymerization of polymer product  |
| $E_i$         | Activation energy of $i$ th reaction ( $\text{J mol}^{-1}$ )                                     |
| $F$           | Mass of liquid in reactor at time $t$ (kg)   |
| $h_i$         | Heat transfer coefficient of liquid ( $\text{kJ m}^{-2} \text{h}^{-1} \text{K}^{-1}$ )           |
| $\Delta H_i$  | Enthalpy change for $i$ th reaction ( $\text{J mol}^{-1}$ )                                      |
| $k$           | Thermal conductivity of reaction mass ( $\text{kJ m}^{-1} \text{h}^{-1} \text{K}^{-1}$ )         |
| $k_i$         | Rate constants for $i$ th reaction ( $\text{kg mol}^{-1} \text{h}^{-1}$ )                        |
| $k_{l,i}$     | Mass transfer coefficient of component $i$ ( $\text{m h}^{-1}$ )                                 |
| $K$           | Kuhn-Mark-Houwink-Sakurada parameter ( $\text{dl gm}^{-1}$ )                                     |



|                    |  |
|--------------------|--|
| $K_i$              | Equilibrium constants for $i$ th reaction  |
| $[M^v]$            | Concentration of caprolactam in vapor phase ( $\text{mol m}^{-3}$ )  |
| $M_n$              | Number average molecular weight  |
| $M_w$              | Weight average molecular weight  |
| $n$                | Rate of rotation of stirrer ( $\text{rev min}^{-1}$ )  |
| $N_{j-i}$          | Normality of the $i$ th solution with $j$ th solute  |
| $[N^v]$            | Concentration of nitrogen in vapor phase ( $\text{mol m}^{-3}$ )   |
| $N_{\text{Re}}$    | Reynolds number  |
| $N_{\text{Sc}}$    | Schmidt number   |
| $N_{\text{Sh}}$    | Sherwood number  |
| $P$                | Total pressure (kPa)   |
| $P_i^{\text{sat}}$ | Vapor pressure of component $i$ (kPa)  |
| $Q$                | Polydispersity index   |
| $r_i$              | Net forward rate for $i$ th reaction ( $\text{mol kg}^{-1} \text{h}^{-1}$ )                                    |
| $R$                | Universal gas constant ( $\text{kPa m}^3 \text{mol}^{-1} \text{K}^{-1}$ or $\text{J mol}^{-1} \text{K}^{-1}$ ) |
| $R_{vm}$           | Rate of evaporation of caprolactam ( $\text{mol h}^{-1}$ )   |
| $R_{vw}$           | Rate of evaporation of water ( $\text{mol h}^{-1}$ )   |
| $[S_i]$            | Concentration of linear oligomers in liquid ( $\text{mol kg}^{-1}$ )   |
| $\Delta S_i$       | Entropy change for $i$ th reaction ( $\text{J mol}^{-1} \text{K}^{-1}$ )                                       |
| $t$                | Time (h)   |
| $t_f$              | Total reaction time (h)  |
| $T$                | Temperature (K)  |
| $T_r$              | Reference temperature (= 473.15 K)   |

|         |  |
|---------|--|
| $U$     | Overall heat transfer coefficient ( $\text{kJ h}^{-1} \text{ m}^{-2} \text{ K}^{-1}$ ) |
| $V_g$   | Volume of the vapor space ( $\text{m}^3$ )   |
| $V_T$   | Rate of the vapor escape from the reactor ( $\text{mol h}^{-1}$ )                      |
| $[W]$   | Water concentration in liquid ( $\text{mol/kg mixture}$ )                              |
| $[W^v]$ | Water concentration in vapor ( $\text{mol m}^{-3}$ )                                   |

### Greek symbols

|             |  |
|-------------|--|
| $\alpha$    | Kuhn-Mark-Houwink-Sakurada parameter   |
| $\chi_i$    | Mole fraction of $i$ th species  |
| $\gamma_i$  | Activity coefficient of $i$  |
| $\eta$      | Viscosity of liquid mixture ( $\text{Pa s}$ or poise; $1 \text{ poise} = 10^{-1} \text{ Pa s}$ )       |
| $[\eta]$    | Intrinsic viscosity of $\epsilon$ -caprolactam-nylon-6 mixture ( $100 \text{ kg mixture/kg polymer}$ ) |
| $\zeta_i$   | Total mol of $m$ ( $i = 1$ ), $w$ ( $i = 2$ ) or both ( $i = 3$ ) vaporized to time $t$ (mol)          |
| $\lambda_i$ | Latent heat of vaporization of $I$ ( $\text{kJ mol}^{-1}$ )  |
| $\mu_i$     | Moments of the $S_n$ distribution  |
| $\mu_n$     | Number average chain length ( $\equiv \mu_1/\mu_0$ )   |
| $\rho$      | Density of the liquid mixture ( $\text{kg m}^{-3}$ )   |

### Subscripts/superscripts

|      |                    |
|------|--------------------|
| b    | Bubble             |
| expt | Experimental value |
| f    | Free surface       |
| j    | Jacket             |
| l    | Liquid             |
| m    | Monomer            |

o      Feed conditions  
simuln Simulation values  
theor   Theoretical values  
v      Vapor  
w      Water

## ABSTRACT

This study deals with the hydrolytic step-growth polymerization of  $\epsilon$ -caprolactam to produce nylon-6 in a semi-batch reactor at near industrial conditions.  $\epsilon$ -caprolactam is polymerized in a 1.5-lit SS reactor at three different initial water concentrations, 3.45 % (by mass), 2.52 %, and 4.43 %, respectively. During the polymerization, the values of the temperature and the pressure are controlled and noted down *manually*. Samples of the liquid reaction mass are taken out from the reactor at different times and analyzed. The monomer conversions are obtained gravimetrically as well as using gas chromatography. It is observed that these two experimental techniques give superposable results. It is also seen that these experimental results match the simulated values quite well. The samples are also analyzed for the degree of polymerization using amide and acid end-group concentrations. The values obtained are not superposable (possibly because of chain scission in one of the techniques). There is also a considerable mismatch between the experimental results on DP and the simulated values. This suggests that the correlations for the activity coefficients, tuned using data on a large-scale industrial reactor, do not apply to the smaller reactor and indicates the need for developing improved correlations using extensive experimental data on the laboratory scale reactor.

## CHAPTER 1

### INTRODUCTION

Nylons are polymers characterized by the polyamide (-CONH-) bond. In particular, nylon-6 is a linear synthetic polyamide, which has six carbon atoms per repeat unit. It is prepared from  $\epsilon$ -caprolactam. Nylon-6 is extensively used in the production of various articles. About 70 % of the production is used in the form of fibers in carpets, hosiery, fishing nets, ropes, cords, etc. In addition, considerable quantities of nylon-6 are used in molding, extrusion, and casting operations for the manufacture of injection and blow molded objects, tubing, pipes, tapes, sheets, rods and monofilaments. The latter are used in automobiles, appliances, machinery, electrical and consumer goods. This rather wide spectrum of applications can be explained by the particular combination of properties that characterizes this polymer. The properties of the polymer depend on the method of preparation as well. There are two routes for the polymerization of  $\epsilon$ -caprolactam:<sup>1,2</sup>

1. Ionic chain growth mechanism
2. Hydrolytic step growth polymerization

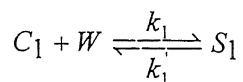
In ionic chain growth polymerization, polymerization can be carried out below the melting point of nylon-6 (220 °C) and can be used for the production of large cast articles. The molecular weight of the polymer formed in anionic polymerization is usually much higher than that obtained by the hydrolytic polymerization route. The anionic process, however, has not yet become popular industrially due to difficulties in controlling the reaction. Dry atmosphere is required to carry out anionic polymerization. The cationic process is not popular as the monomer conversion and the attainable

molecular weights are not adequate for practical uses. Most of the nylon-6 producing plants commonly use the hydrolytic polymerization process. This process consists of the polymerization of  $\epsilon$ -caprolactam ( $C_1$  or CL) in the presence of water (W) at temperatures ranging from 230  $^{\circ}\text{C}$  to 280  $^{\circ}\text{C}$ . Water is used to open the  $\epsilon$ -caprolactam ring (reversibly) to give a linear molecule, amino caproic acid (ACA,  $S_1$ ; see Table 1). Polymerization then proceeds by the step growth mechanism to give linear polymers ( $S_n$ ), with water as the condensation by-product. In addition to these reactions, the amino end group of any linear polymer molecule ( $S_n$ ) can also open the  $\epsilon$ -caprolactam ring reversibly. This is the polyaddition reaction. The linear dimer,  $S_2$ , however, can cyclize reversibly to form cyclic dimer ( $C_2$ ). The amino end group of any linear polymer ( $S_n$ ) can attack a molecule of the cyclic dimer and add it on, giving a longer linear molecule ( $S_{n+2}$ ). Higher cyclic oligomers ( $C_3$ ,  $C_4$ , . . .) are also formed, but these are not included in Table 1 since their concentrations are smaller, and data on their rates of formation are not available.

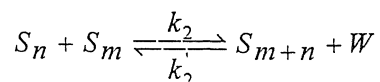
Hydrolytic polymerization is usually carried out until near-equilibrium conditions. The quantity of monomer present in the equilibrium polymer depends upon the reaction temperature and the amount of water present in the reaction mass. Under industrial conditions, the amount of residual monomer present in the polymer is about 8-9 %, while that of the cyclic oligomers is about 3-6 %. Since the subsequent processing of the polymer is adversely affected by the presence of the monomer, water and the cyclic oligomers, it is necessary to remove these. This is achieved by a hot water extraction process or vacuum evaporation.

Table 1: Kinetic scheme of nylon-6 polymerization

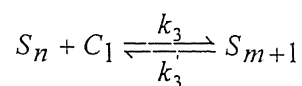
1. Ring Opening:



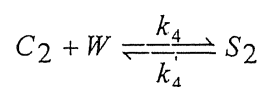
2. Polycondensation:



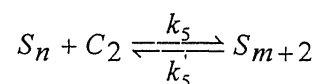
3. Polyaddition:



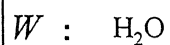
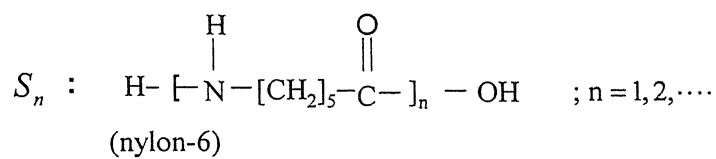
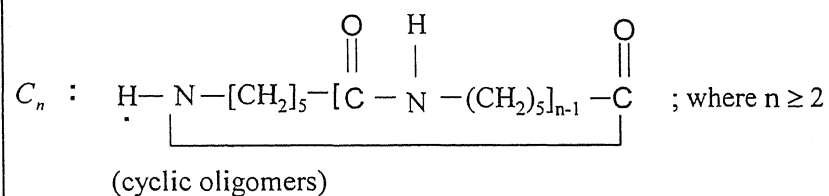
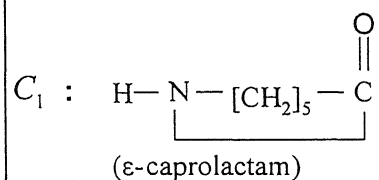
4. Ring Opening of Cyclic Dimer :



5. Polyaddition of Cyclic Dimer:



The chemical structures are as follows:



Several studies have been reported on nylon-6 polymerization. Reimschuessel<sup>1</sup> was among the early workers in the field. This group described the mechanism and the kinetics of polymerization and reported values of the several rate constants. Their constants, however, were estimated using *some* experimental data. They did not measure the concentration of aminocaproic acid (they estimated the equilibrium  $S_1$  concentration from the equilibrium end-group concentration and the number-average degree of polymerization by assuming a Flory-Schulz distribution). In fact, very little data on the concentration of  $S_1$  exists under a variety of experimental conditions except those of Hermans<sup>3</sup> et al., and that too under comparatively limited conditions. Tai et al.<sup>4-7</sup> were probably the first to report detailed data on the effect of temperature and the initial water concentration on the concentration of  $S_1$  using high performance liquid chromatography (as well as the concentration  $C_1$ , end-groups,  $M_n$ , etc.). They fitted their experimental results and provided improved correlations for the several rate constants. These are listed in Table 2 along with recently updated values<sup>8</sup> for some kinetic parameters.

Gupta and coworkers<sup>2,8-11</sup> have reported several studies on the modeling and optimization of industrial nylon-6 reactors. One of these is an industrial semi-batch reactor, in which  $C_1$  and W vaporize and build up the pressure in the (closed) space above the liquid reaction mass. The vapors are released later in a programmed manner and the pressure reduces. This controls the liquid phase concentration of W, and thus controls the rate of polymerization, with the W concentration being high initially (to speed up the ring opening) and lower later on (to drive the polymerization forward). Unfortunately, because of the absence of sufficient industrial data for this reactor, several empirical



Table 2: Rate and equilibrium constants:<sup>4,8</sup>

$$k_i = k_i^0 + k_i^c[-COOH] \quad (i=1, 2, \dots, 5); \quad k_i^j = A_i^j \exp\left(\frac{-E_i^j}{RT}\right) \quad (j=0, c)$$

$$K_i = \exp\left[\frac{\left(\Delta S_i - \frac{\Delta H_i}{T}\right)}{R}\right] \quad (i=1, 2, \dots, 5)$$

| $i$            | $A_i^0$<br>$\left(\frac{kg}{mol\ h}\right)$ | $E_i^0$<br>$\left(\frac{J}{mol}\right)$ | $A_i^c$<br>$\left(\frac{kg^2}{mol^2\ h}\right)$ | $E_i^c$<br>$\left(\frac{J}{mol}\right)$ | $\Delta H_i$<br>$\left(\frac{J}{mol}\right)$ | $\Delta S_i$<br>$\left(\frac{J}{mol\ K}\right)$ |
|----------------|---|---|---|---|--|---|
| 1              | $5.9874 \times 10^5$                        | $8.3198 \times 10^4$                    | $4.3075 \times 10^7$                            | $7.8703 \times 10^4$                    | $8.0268 \times 10^3$                         | $-3.2997 \times 10^1$                           |
| 2              | $1.8942 \times 10^{10}$                     | $9.7389 \times 10^4$                    | $1.2114 \times 10^{10}$                         | $8.6504 \times 10^4$                    | $-2.4883 \times 10^4$                        | $3.9496 \times 10^0$                            |
| 3 <sup>a</sup> | $2.8558 \times 10^9$                        | $9.5606 \times 10^4$                    | $1.6377 \times 10^{10}$                         | $8.4148 \times 10^4$                    | $-1.6923 \times 10^4$                        | $-2.9068 \times 10^1$                           |
| 3 <sup>b</sup> | $2.8558 \times 10^9$                        | $9.5606 \times 10^4$                    | $1.6377 \times 10^{10}$                         | $7.5733 \times 10^4$                    | $-1.5231 \times 10^4$                        | $-2.9068 \times 10^1$                           |
| 4              | $8.5778 \times 10^{11}$                     | $1.7577 \times 10^5$                    | $2.3307 \times 10^{12}$                         | $1.5652 \times 10^5$                    | $-4.0176 \times 10^4$                        | $-6.0766 \times 10^1$                           |
| 5              | $2.5701 \times 10^8$                        | $8.9141 \times 10^4$                    | $3.0110 \times 10^9$                            | $8.5374 \times 10^4$                    | $-1.3263 \times 10^4$                        | $-2.4384 \times 10^0$                           |

<sup>a</sup> values of Tai et al.<sup>4</sup>

<sup>b</sup> values of Wajge et al.<sup>8</sup>

equations had to be used, particularly those associated with the rates of vaporization of  $C_1$  and  $W$ , and the associated parameters tuned. In fact, very little experimental/industrial data are available in the open literature to estimate the rates of evaporation for *any* polymerization reactor. The present study attempts to generate some detailed, albeit preliminary, experimental data on a 1.5-liter stainless steel nylon-6 reactor in which vaporization takes place and the vapor is released to give a desired pressure history. Samples of the liquid (as well as the vapor) are taken at different times during the polymerization. The liquid samples are analyzed using gas chromatography, gravimetric analysis, and end group analysis. The molecular weight of the polymer and the conversion of  $C_1$  are estimated. The gas is analyzed using gas chromatography to estimate the concentration of the  $C_1$  in the vapor phase. This study will help to generate more detailed data than what is currently available, and will help to improve the earlier model of Wajge et al.<sup>8</sup>

## CHAPTER 2

### EXPERIMENTAL DETAILS

#### Design of the Reactor:

The reactor used in this study is specially designed to carry out the polymerization of nylon-6 at temperatures of about 250<sup>0</sup>C. A 1.5-liter semi-batch 304-SS reactor is used. The reactor is mounted on a movable aluminum trolley. A 2000 W electric heater is wound around the reactor. This is insulated on the outside with asbestos rope (see Fig. 1). There are several SS pipes connected to the reactor head. One (0.64 cm  $\phi$ ) is fitted with a needle valve ( $N_2$  in Fig. 1), which controls the rate of release of vapor and, thus, the pressure inside the reactor. A gas-collector, fitted with two gate valves at its two ends, as well as a septum at the middle, is connected in this line. The latter allows taking samples with a gas-tight syringe. The outlet of the gas-collector is connected to another 0.64 cm  $\phi$  SS tube, which vents the vapor to the outside. The gas-collector and the inlet and outlet SS tubes are maintained at high temperatures by winding a 250 W heating tape around them. Two more openings in the reactor head include: one for feeding nitrogen to the reactor through the needle valve ( $N_1$  in Fig. 1) [the nitrogen exits through the line carrying the gas sampling tube through the needle valve ( $N_1$ ) during purging], and the other for charging the monomer. This opening is closed by a SS stopper. The reactor is fitted with a pivoted anchor stirrer, a thermo well, and a pressure gauge (0-14 kg/cm<sup>2</sup>; on the inlet nitrogen line). A calibrated J-type (iron-constantan) thermocouple is used to measure the temperature of the liquid inside the reactor. The temperature of the reaction mass is controlled by a time-proportioned PID controller (Fusi Electricals, Japan). The

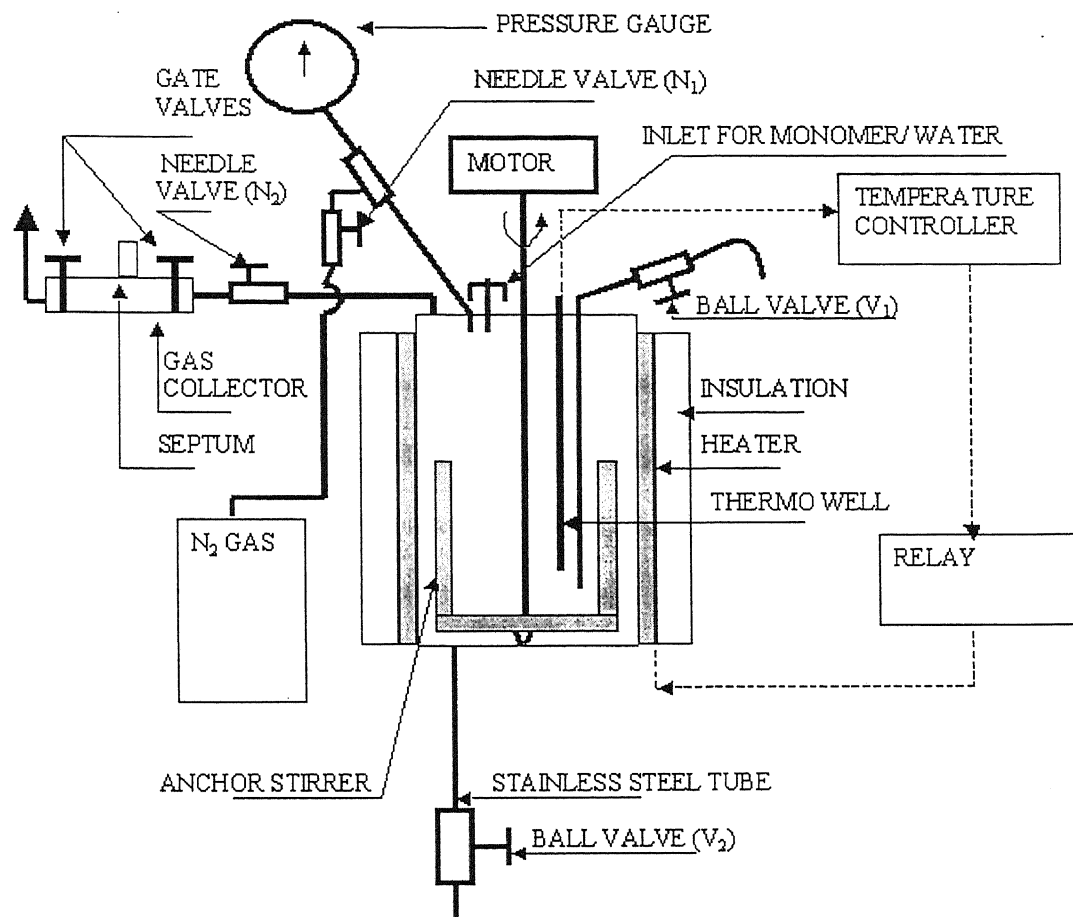


Fig.1 Schematic of the 1.5-liter semi-batch SS reactor assembly used in the present study

stirrer is operated by a 0.187 kW motor and its speed is measured by a digital tachometer. A ball valve ( $V_1$ ) is fitted on another SS tube on the reactor head. This tube is open at the bottom and dips into the reaction mass. This, too, is surrounded by a 250 W heating tape and is used for taking out samples *initially* when the reaction mass is less viscous. There is an opening in the bottom of the reactor to take out polymer samples at *later stages* of reaction, when the reaction mass is more viscous, through a 1.4 cm O.D. SS pipe, with a ball valve ( $V_2$ ). This is also wrapped with a 250 W heating tape. The first two (initial) samples are taken out through the ball valve,  $V_1$ , while the remaining samples are taken out through the ball valve,  $V_2$ . This is because the viscosity of the polymer in the early stages is low and the pressure inside the reactor is quite high. If these early samples are taken through the valve,  $V_2$ , it leads to a very rapid and complete draining of the liquid from the reactor. The liquid samples are taken out from the reactor over short periods of time, in empty beakers that have been chilled in ice water (before and after collection). While the samples come out, some amount of vapor flashes to the atmosphere (more in the initial samples). Improved procedures are required for this. The entire reactor assembly is kept inside a vented hood so that toxic vapors ( $\text{NO}_2$  from the oxidation of  $\text{C}_1$ , etc.) are removed.

### **Polymerization and Analysis:**

#### **Raw Materials:**

##### **$\epsilon$ -Caprolactam:**

$\epsilon$ -Caprolactam and water are the main raw materials for the production of nylon-6. GC grade (purity > 98%) caprolactam (Fluka, Belgium) is used without further purification.

**Physical Properties:**

1. Melting point:  $69.2^{\circ}\text{C}$
2. Boiling point:  $270.8^{\circ}\text{C}$
3. Viscosity of liquid:  $9 \times 10^{-3} \text{ Pa-s}$  at  $78^{\circ}\text{C}$
4. Heat of fusion of solid:  $121.336 \times 10^3 \text{ J/kg}$
5. Heat of vaporization of liquid:  $485.344 \times 10^3 \text{ J/kg}$
6. Relative density of solid: 1.1
7. Solubility of solid in water:  $0.82 \times 10^{-3} \text{ kg/cm}^3$  at  $20^{\circ}\text{C}$
8. Flash point:  $110^{\circ}\text{C}$
9. Specific heat of solid:  $2.108736 \times 10^3 \text{ J/kg-K}$
10. Heat of polymerization of liquid:  $20 \text{ cal/mole}$
11. Vapor pressure of solid:  $0.0025 \times 10^2 \text{ Pa}$  at  $20^{\circ}\text{C}$

**Operational Hazards:**

1. It is a white crystalline compound which decomposes on heating forming toxic vapors of  $\text{NO}_2$ .
2. It irritates the eyes and the respiratory tract. At room temperature, a harmful vapor concentration is likely to develop. It may be absorbed in the body by ingestion and inhalation of dust or vapor.

**Other chemicals used (for analysis):**

1. **Meta-cresol:** Meta-cresol (Loba Chemicals, Mumbai, India) having a purity greater than 98 % is used. Samples are stored in a dark place.
2. **Benzyl alcohol:** Extra-pure grade benzyl alcohol (S. D. Fine Chemicals, Mumbai, India) having a purity of greater than 98.5 % is used in the analysis. The acid

content should be below 0.05 %. The inherent acidity is accounted for by blank titration so as to get correct results.

3. **Ethylene Glycol:** Ethylene glycol (Qualigens, Mumbai, India) having a purity greater than 98 % is used. Its acidity should be below 0.01%. The correct normality of a glycol-KOH solution used for analysis is found by titrating with a standard base solution.

#### **Polymerization:**

A measured amount of solid  $\epsilon$ -caprolactam ( $> 500$  g) is put in the reactor in the tilted position so that the solid does not fill up the seat of the pivot at the bottom of the stirrer. The reactor head is then placed on top, and sealed. The remaining  $C_1$  and the prescribed amount of  $W$  is introduced through the opening in the head, which is then closed using the SS stopper. The contents of the sealed reactor are then flushed four times using nitrogen (Grade-I, Pawan Gases, Kanpur, India). Initially, a (gage) pressure of  $1.0 \times 10^5$  Pa of nitrogen is maintained in the reactor. The reactor is then heated (over about 38 min) to  $245^\circ\text{C}$ . Thereafter, the temperature is maintained constant. The temperature of the molten reaction mass is measured by a calibrated J-type thermocouple. The  $\epsilon$ -caprolactam starts melting as the temperature increases. Since the melting point of  $\epsilon$ -caprolactam is  $69^\circ\text{C}$ , the stirrer is started as soon as the temperature of the reaction mass goes above about  $69^\circ\text{C}$ . The stirrer speed is maintained at 60 rpm. As the reaction proceeds, the pressure builds up in the vapor space as  $\epsilon$ -caprolactam and water vaporize while there is no release of vapors. High water concentrations are required at the beginning of the process, while low water contents are needed towards the end so as to drive the poly-condensation reaction forward and obtain nylon-6 having a high degree of

polymerization. To achieve this, the reactor is operated in five different stages. In the first stage, the pressure is allowed to build up to a set value. In the second stage, the needle valve ( $N_2$ ) (see Fig. 1) is opened in such a way that the pressure remains almost constant for a desired period. In the third, fourth and fifth stages, the needle valve ( $N_2$ ) is operated in such a way that the pressure drops (with three different slopes with respect to time). The desired pressure history (somewhat similar to that used industrially<sup>8</sup>) is maintained in the reactor by *manual* control of the valve,  $N_2$ .

#### **Temperature Control:**

Temperature control is an important aspect in any polymerization. A time-proportioned PID controller is used to control the temperature of the reaction mass. The temperature is measured by a calibrated J-type thermocouple inserted in the thermo well. The controller is operated in the auto-tuned mode. Auto tuning is done using silicone oil (370-390 mPa-s at 20 °C) in the reactor at 200 °C (instead of at 245 °C to be used for nylon-6 polymerization). This is because during the tuning, the reactor experiences an overshoot in the temperature of about 100 °C, and if the auto tuning was done at 245 °C, the temperature would go up beyond 310 °C and damage the Teflon packing in the reactor head. Auto tuning should really be carried out using caprolactam in the reactor at 245 °C. However, it is difficult to auto tune the reactor with caprolactam because of vaporization, and subsequent increase in the pressure. The temperature of the nylon-6 polymerizing system is controlled by providing the set point in two steps. In the first step, the set point is given as 230 °C. This leads to an overshoot of about 25 °C. As soon as the temperature reaches 220 °C, the set point is changed to 245 °C. It has been found that



with this approach, the reactor stabilizes at 245 °C quite smoothly, and there is no overshoot. The auto tuned parameters used are given below:

1. Proportional band (P): 11.6
2. Integral action time (I): 906 s
3. Derivative action time (D): 174.3 s
4. Proportional time cycle (TC): 30 s
5. Insensitive zone (HYS): 2 %
6. Other parameters can be changed depending upon the requirement by taking the guidance of the manual provided by the manufacturer.

#### **Cleaning of the reactor:**

As soon as the polymerization is over, the pressure in the reactor is increased to about 1000 kPa using nitrogen, so as to force out the molten reaction mass through the heated tube at the bottom. Sometimes it is not possible to drain out the molten polymer from the bottom tube because of its high viscosity. When this happens, the reactor is cooled for 3 hr so that the reaction mass solidifies. The reactor is then heated till the thermocouple measures about 100 °C. This corresponds to a reactor wall temperature of about 250 °C. This is sufficient to melt the solidified polymer *near the wall*, and the reactor head can easily be pulled out along with the solidified reaction mass and the reactor internals. The embedded stirrer rod is then unscrewed from the top, and the upper part of the rod is slipped out of the reactor head, leaving the impeller and the bottom part of this rod buried inside the solid. This is done so as to avoid damage to the packing, etc., during cleaning. The solid polymeric mass is then crushed *carefully* so as to avoid damage to the reactor internals buried inside. Before crushing the polymer, the height of

the polymer is measured so as to obtain the volume of the vapor space. M-cresol is then added to the reactor and the reactor sealed with the head and kept for three days keeping the stirrer on so that residual polymer in the reactor dissolves. The reactor is finally cleaned using water, while wearing gloves as well as a mask. The used nylon-6 solution in m-cresol is kept in bottles and disposed off. If the polymer chokes the sampling tubes (at the bottom as well as the top), it is removed by drilling, followed by cleaning with m-cresol and, later on, with water.

**Guidelines for conducting the experiment:**

1. The temperature controller is checked to see if it is working properly by cross checking it with a thermometer. Water is taken in the reactor and is heated to about 80 °C. The head is removed and a thermometer inserted immediately to cross check the temperature.
2. The set-up is run with water at 80 °C to check the valves, controller, etc.
3. Safety glasses, apron, and a mask must be used while pouring and measuring the concentration of  $\epsilon$ -caprolactam, as it is highly irritating to the eyes and the respiratory tract. It may be absorbed in the body by ingestion of dust or vapor.
4. Nitrogen is purged for 5 min in the reactor, so that negligible amounts of air are present in the reactor during polymerization.
5. The exhaust fan in the hood is kept on during the entire experiment. This is to further ensure safety since small amounts of air may still be present in the reactor (irrespective of the purging of nitrogen) and cause the decomposition of caprolactam on heating to form some toxic vapors of  $\text{NO}_2$ .

6. The first two samples of the reaction mass are taken from the upper sampling tube (because, initially, the viscosity is low and the pressure inside the reactor is high). If the bottom tube is used initially, the entire contents of the reactor may be quickly drained out unless one is extremely careful.
7. The remaining samples are taken from the bottom sampling tube, as the diameter of this tube is larger (1.4 cm O.D) and the polymer is quite viscous.
8. All the samples are collected in 100 ml beakers immersed in cold water (20 °C) to quench the polymerization.

### **Analytical Procedure:**

#### **Gravimetry:<sup>4</sup>**

The solid polymer samples collected in the beakers are crushed to a powder by a hammer, or shaved by a drill. The weighed samples are then extracted with 20 times their weight of freshly distilled water at 80°C for 4 hr in an electric oven, after which they are filtered onto weighed filter papers (No. 42, Whatman, Maidstone, U. K.) and dried to a constant weight by heating to 105 °C at 1 atm pressure in an electric oven. Under these conditions, extraction equilibrium can be assumed to have been achieved, and the hydrolysis of  $C_1$  to  $S_1$  is negligibly small. The total hot water-soluble content is equal to the loss in weight of the sample caused by extraction. The  $C_1$  content in the aqueous solution is also determined by gas chromatography (described later).

#### **Molecular Weight Determination:**

##### **Viscometry:**

Dilute solution viscometry is extensively used to determine the molecular weight of polymers. The Kuhn-Mark-Houwink-Sakurada equation:

$$[\eta] = KM^a \quad (1)$$

is used. Values of the two constants,  $K$  and  $a$  are reported in Table 3<sup>12</sup> for different solvents and temperatures. The viscosities of dilute polymer solutions are measured in m-cresol at 30 °C using an Ubbelohde viscometer (No.1A, Vensil, Bangalore, India) that has a flow time,  $t$ , greater than about 100 s for the pure solvent. A known amount of the

Table 3: Values of the Kuhn-Mark-Houwink-Sakurada parameters<sup>12</sup>

| Solvent  | T, °C | $a$   | $K$ (dl/g)            | $M_n^*$ (g/mol)                     | $M_w^+$ (g/mol)                     |
|--|-------|-------|-----------------------|-------------------------------------|-------------------------------------|
| 85 % HCOOH   | 25    | 0.82  | $2.26 \times 10^{-4}$ | $5 \times 10^3 - 5 \times 10^4$     |                                     |
| m-cresol   | 25    | 0.745 | $5.26 \times 10^{-4}$ |                                     | $3.0 \times 10^3 - 4.0 \times 10^4$ |
| m-cresol   | 25    | 0.654 | $1.80 \times 10^{-3}$ | $9.0 \times 10^3 - 3.5 \times 10^4$ |                                     |
|  |       | 0.735 | $5.58 \times 10^{-4}$ |                                     | $5.0 \times 10^3 - 6.0 \times 10^4$ |
| m-cresol   | 30    | 0.53  | $3.04 \times 10^{-5}$ | $< 4.3 \times 10^3$                 |                                     |
| 96 % H <sub>2</sub> SO <sub>4</sub>  | 25    | 0.780 | $3.32 \times 10^{-2}$ | $6.0 \times 10^2 - 1.0 \times 10^5$ |                                     |
| 96 % H <sub>2</sub> SO <sub>4</sub>  | 25    | 0.79  | $3.31 \times 10^{-2}$ |                                     | $2.7 \times 10^4 - 5.7 \times 10^4$ |
| 95.6 % H <sub>2</sub> SO <sub>4</sub>  | 20    | 0.79  | $5.12 \times 10^{-2}$ | $8.8 \times 10^3 - 1.8 \times 10^4$ |                                     |
| TFP <sup>α</sup> -H <sub>2</sub> O-LiCl<br>(TFP-10% H <sub>2</sub> O-<br>0.1 M LiCl) | 25    | 0.76  | $3.42 \times 10^{-4}$ |                                     | $9.0 \times 10^3 - 3.5 \times 10^4$ |
| SbCl <sub>3</sub>  | 100   | 1.45  | $2.35 \times 10^{-6}$ |                                     | $9.4 \times 10^3 - 1.0 \times 10^5$ |
| Phenol-DCB <sup>b</sup><br>(1:1 by weight)   | 25    | 0.83  | $2.29 \times 10^{-2}$ |                                     | $2.7 \times 10^4 - 5.7 \times 10^4$ |

<sup>α</sup> Tetrafluoropropanol

<sup>b</sup> 1,2-Dichlorobenzene

\*Equation relates  $[\eta]$  to  $M_n$

<sup>+</sup>Equation relates  $[\eta]$  to  $M_w$

dried polymer sample is first dissolved in m-cresol to prepare solutions of concentrations,  $c$ , ranging from 0.2 to 1 %, and its viscosity is obtained using:

$$\frac{\eta}{\rho} \equiv \nu = At + \frac{B}{t} \quad (2)$$

In Eq. 2,  $A$  and  $B$  are the instrument constants,  $\rho$  is the solution density and  $\nu$  is the kinematic viscosity. In the above equation, the first term on the right represents the Hagen-Poiseuille law and the second corrects for kinetic energy losses associated with the fluid leaving the capillary. Usually, the constants  $A$  and  $B$  are supplied by the manufacturer, or are obtained by calibration with standard liquids like water at two different temperatures. Normally, the last term in Eq. 2 is negligible. In addition, the densities of dilute polymer solutions differ very little from that of the solvent, and one takes  $\eta$  proportional to  $t$ . Thus

$$\begin{aligned} \frac{\eta}{\eta_s} &\equiv \frac{t}{t_s} \equiv \eta_r = \text{relative viscosity} \\ \eta_{inh} &\equiv \frac{\ln \eta_r}{c} = \text{inherent viscosity} \\ \eta_{sp} &\equiv \left( \frac{\eta}{\eta_s} - 1 \right) = \text{specific viscosity} \end{aligned} \quad (3)$$

where  $t_s$  and  $\eta_s$  are the flow time and the viscosity of the pure solvent, respectively.

Thus, values of the inherent viscosity and the relative viscosity are obtained over the concentration range of up to about 2 % polymer solution. These values are then plotted on the same graph against the polymer concentration. A double-extrapolation procedure<sup>19</sup>

is used and best-fit straight lines for data on  $\frac{\eta_{sp}}{c}$  and  $\eta_{inh}$  vs.  $c$  are extrapolated to give a

common intercept at  $c = 0$ . The intercept is the intrinsic viscosity,  $[\eta]$ . This is based on the following equations:

$$\begin{aligned}\frac{\eta_{sp}}{c} &= [\eta] + k' [\eta]^2 c \\ \eta_{inh} &= [\eta] + k'' [\eta]^2 c\end{aligned}\tag{4}$$

$[\eta]$  is used in the Kuhn-Mark-Houwink-Sakurada Eq. 1 with the values of  $K$  and  $a$  to obtain the molecular weight. The normal concentration range (0-1.0 g/dl) in meta-cresol is sufficient for the higher molecular weight polymer but for the low molecular weight polymer produced initially, concentrations of as high as 5 g/dl may need to be used. Different values  $K$  and  $a$  have been reported<sup>14</sup> for different ranges of molecular weights.

#### **End-group Analysis:**

This is a very important method,<sup>14-15</sup> particularly for the determination of the molecular weights of condensation polymers. The molecular weights of linear condensation polymers are normally below about 20,000, and end-group methods are most accurate for such ranges. It is possible to estimate the concentration of the end-groups by chemical analysis and use these to estimate the value of the number average molecular weight,  $M_n$ , of linear polymers. This method has the advantage of being a fundamental method, not requiring any calibration against other methods (e.g.,  $[\eta]$ ).

#### **Carboxyl End-group:**

The most useful methods for nylons are based on titration against an alkali in a suitable alcoholic solvent, as proposed by Waltz and Taylor.<sup>17</sup> Polyamides, like nylon-6 and nylon-66, are soluble in hot benzyl alcohol and the titration must, therefore, be carried out in this. As nylon-6 dissolved in hot benzyl alcohol remains in solution even

after cooling, this technique can be used for estimation, as described below. The hot benzyl alcohol solution may be titrated conductometrically, or with a visual indicator. Again, it can be titrated potentiometrically at room temperature.

**Apparatus:**

A three necked round bottom flask is used. Two of the necks are fitted with valves, and are used for input and outlet of nitrogen, while the third neck is used for pouring the polymer and the benzyl alcohol. The flask is maintained at 150 °C by using a constant temperature oven from which it can readily be removed for titration.

**Reagents:**

The solvent used for nylon-6 is pure benzyl alcohol. It should be colorless, boil in the range of 202-206°C, and have a low content of benzaldehyde. A test volume of solvent (60 ml) should give a blank titre of less than 0.3 ml of 0.02 N glycolic potassium hydroxide and the phenolphthalein color change should be sharp. Perfumery grade benzyl alcohol is normally suitable for this purpose. The base used for the titration of the nylon-6 solution is potassium hydroxide in ethylene glycol. 0.02 N solution of KOH is prepared by diluting 0.14 gm of KOH in 100 ml of glycol. It should be kept in mind that the normality of the glycol solution should be fixed by standardization regularly, using a standard solution of 0.025 N aqueous hydrochloric acid. The indicator is 1 % phenolphthalein in methanol. The KOH-glycol solution must be protected from atmospheric carbon dioxide.

**Procedure:**

About 0.5 g of the finely divided sample is weighed and added to the three-necked round bottom flask together with 60 ml of benzyl alcohol. An inert atmosphere is



maintained by flushing with nitrogen for 2 min. The flask is then heated in a constant temperature oven maintained at 150 °C. As soon as the sample has dissolved, the solution is rapidly cooled to 60 °C by placing the flask in a cold water bath while stirring. About 20 ml of (2:1) methanol/water solution are added to reduce the viscosity and the solution is then titrated with 0.025 N potassium hydroxide solution in ethylene glycol from a micro-burette, with phenolphthalein as indicator. The usual blank titration (of pure benzyl alcohol against KOH-glycol solution) is performed so as to get rid of the inherent acidity.

It is also possible to titrate the nylon-6-benzyl alcohol solution with HCl to determine the amine group concentration (using bromophenol blue as indicator) using this procedure. However, the amine end-groups are better determined by the titration method described below.

#### **Amide end-group:**

Methods of estimation of this group include direct titration with acid. Polyamides are generally titrated with phenolic solvents. The more general procedure of Waltz and Taylor<sup>17</sup> using a phenolic solvent is described below. The end-point can be determined conductometrically, or with a chemical indicator.

#### **Apparatus:**

A 250 ml beaker is sufficient. A micro-burette of 5 ml capacity with 0.01 ml graduations is suitable for titration.

#### **Reagent:**

The methanol used in the solvent must be pure. 40 ml m-cresol is used for dissolving the polymer and 20 ml of methanol and 10 ml of water are added to maintain the

homogeneity of the solution. The titrant is 0.05 N aqueous hydrochloric acid and the indicator is a neutral 0.1 per cent solution of thymol blue in water.

**Procedure:**

About 0.4 g of the dried sample are weighed and transferred to the solution beaker and 40 ml of meta-cresol is added. As soon as the polymer dissolves 20 ml of methanol is added along with 10 ml of distilled water to make the solution homogeneous. 0.2 % thymol blue is added and the solution titrated with a 0.02 N HCl solution to a pink end-point. The usual blank titration (m-cresol-methanol-water solution titrated against HCl) should also be performed.

**Equation used for calculation:<sup>16</sup>**

$$M_n = \frac{(\text{sample weight} \times 1000)}{(\text{titer, ml,} \times \text{normality})} \quad (5)$$
$$x_n = \frac{M_n}{M_0} ; \text{ where } M_0 \text{ is the molecular weight of a repeat unit}$$

**Precautions:**

1. All the glassware should be free from moisture. The burette and all glassware including the three-necked flask are rinsed with methanol and then dried in an oven at 100 °C.
2. All the chemical bottles are kept sealed so that benzyl alcohol and meta-cresol are not oxidized.
3. All the samples dissolved in the m-cresol are kept in a dark place.
4. Blank titration should be performed before using the benzyl alcohol. If the blank titre is above about 0.3 ml of 0.025 N KOH solution in glycol then the benzyl alcohol should not be used.

5. Polymer sample should be well dried before use.
6. For acid group titration, the HCl-water solution must be standardized with standard KOH-water solution. The above acid solution should be used to standardize the KOH-ethylene glycol solution for the amide group as the glycol generally has some acidity.
7. The KOH-glycol solution is kept away from atmospheric carbon dioxide by keeping it in an air tight flask.
8. The three-necked flask is cleaned with m-cresol, then with water and then rinsed with methanol, and dried before the next analysis.
9. Safety glasses, gloves, and mask must be used while working with benzyl alcohol, as it is a severe irritant to the eyes and the respiratory tracts.
10. The exhaust fan in the hood, as well as two more exhaust fans in the laboratory, should be kept on while working with benzyl alcohol and m-cresol, as they are severe irritants to the respiratory system.
11. Plastic gloves must be used while cleaning the glassware.
12. One glass of milk should be consumed after working with m-cresol and benzyl alcohol.

**Analysis of  $\epsilon$ -Caprolactam:**

**Liquid reaction mass (GC):**

The solution from the hot-water extraction of the polymer is analyzed to get the concentration of the caprolactam in the liquid phase as well as the monomer conversion. A Nucon-5765 (Nucon, New Delhi, India) gas chromatograph (GC) equipped with a dual-flame ionization detector is used for the analysis of CL. The GC was fitted with a 1

m long stainless-steel column, packed with Tenax GC of 80/60-mesh size (Josco, New Delhi, India), and grade-I nitrogen (Sigma Gas Service, New Delhi, India) was used as the carrier gas. In the analysis, the oven temperature was set at 200 °C and the carrier gas flow rate at 30 ml/min. The inlet temperature is maintained at 230°C. A Hamilton (Hamilton, Reno, USA) micro-liter syringe is used for the analysis of the liquid. Generally, 0.5 micro-liter samples are analyzed each time. While inserting the sample, care should be taken to insert the sample in one shot.

The peak for  $C_1$  occurs at 38 s. Initially, a sample of known concentration (made by dissolving a known amount of  $C_1$  in 100 ml of water) is analyzed. The area for this sample is used as a calibration for the calculation of the concentration of the unknown polymer samples. A sample peak is shown in Fig. 2.

#### **Vapor from the reactor:**

As the polymerization proceeds in the reactor, a small amount of caprolactam vaporizes along with water. This vapor is collected in the gas-collector when it comes out of the reactor. The exit tube is maintained at a high temperature (about 150 °C) by use of a heating tape so as to avoid condensation of caprolactam inside the exit tube. The gas sample is taken out from the gas-collector using a Hamilton gas syringe and analyzed using the GC. The problem in this analysis is that the caprolactam and water vapor coming out of the reactor do, indeed, condense in the gas-collector, as well as in the syringe, and correct values of the concentration are not obtained. This problem needs to be solved by redesigning this part of the reactor set-up slightly, and using a GC near the set-up, with heated sampling valves.

A summary of the analysis is given in Fig. 3.

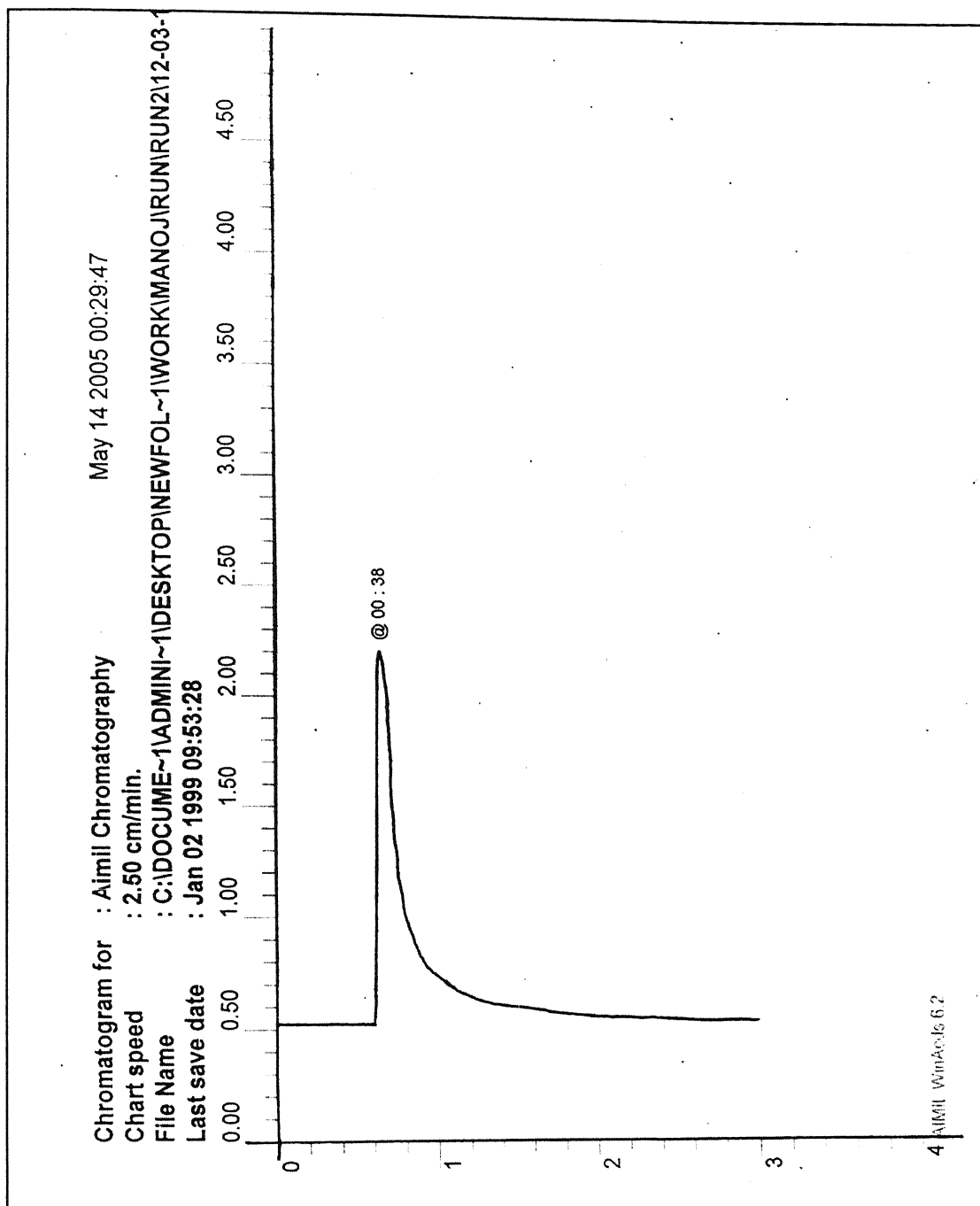


Fig. 2 Caprolactam peak using GC

**Analysis Tree:**<sup>4,12</sup>

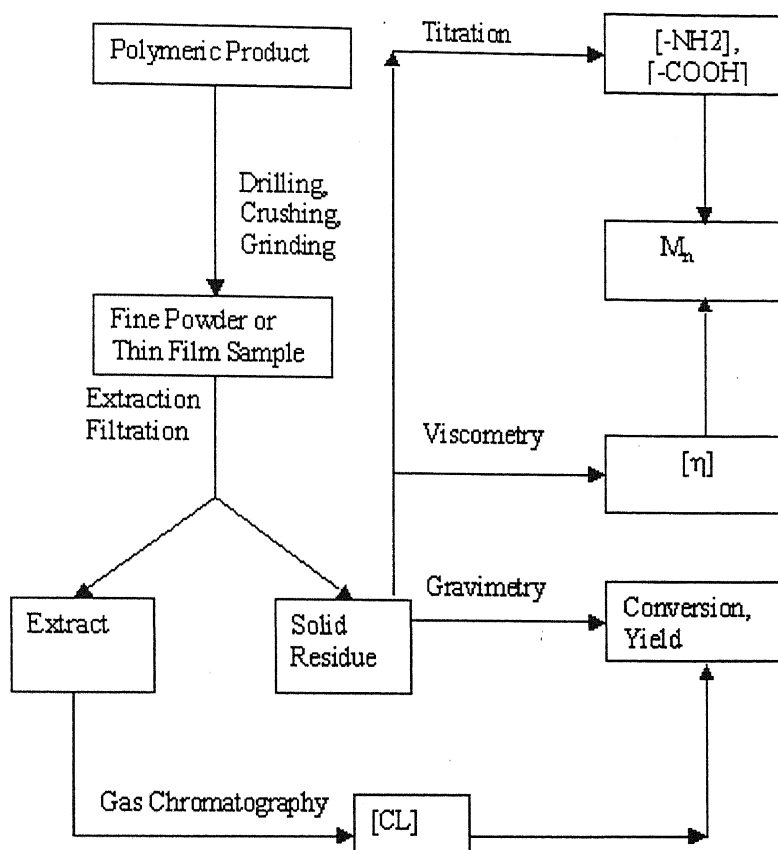


Fig. 3 Schematic diagram of the analysis

## CHAPTER 3

### TUNING OF THE MODEL PARAMETERS

#### **Mechanism and Kinetics:**

The kinetics of the hydrolytic polymerization process has been widely investigated during 1950–1960 by Hermans and Heikens,<sup>3</sup> Reimschuessel<sup>1</sup> and several others. Reimschuessel<sup>1</sup> reviewed most of the early work on the mechanism and kinetics of the hydrolytic polymerization. The reaction mechanism comprises of three main reactions: ring opening of  $\epsilon$ -caprolactam by water to form amino caproic acid, polycondensation, and polyaddition. In addition, there are several important side reactions like the formation of cyclic oligomers ( $C_n$ ;  $n \geq 2$ ), desamination, and peroxidation of  $\epsilon$ -caprolactam. The most important of these are those associated with the cyclic oligomers, since their presence in the product causes problems in processing (e.g., in spinning and molding). The kinetic scheme is given in Table 1 and includes the three main reactions and the reactions associated with the cyclic dimer. The reactions of the higher cyclic oligomers are omitted since precise values of the parameters characterizing their rate constants are not yet available in the open literature. Since the cyclic dimer constitutes a major share of the cyclic oligomers, the kinetic scheme in Table 1 involving only  $C_2$  is quite satisfactory. This table also does not include reactions like decarboxylation, desamination, and peroxidation of the caprolactam.

All the reactions in Table 1 are reversible and catalyzed by the carboxyl end groups of the polymer chains. The reaction rate constants are written as:

$$\begin{aligned}
k_i &= k_i^0 + k_i^c [-COOH] & (i=1, 2, \dots, 5) \\
k_i^j &= A_i^j \exp\left(\frac{-E_i^j}{RT}\right) & (j=0, c) \\
K_i &= \exp\left[\frac{\left(\Delta S_i - \frac{\Delta H_i}{T}\right)}{R}\right] & (i=1, 2, \dots, 5)
\end{aligned} \tag{6}$$

Reimschuessel and Nagasubramanian<sup>18,19</sup> used the Arrhenius form for both  $k_i^0$  and  $k_i^c$ , the rate constants for the uncatalyzed and catalyzed components of  $k_i$ , respectively. They reported values of the activation energies and the frequency factors. The equilibrium constants are expressed in terms of the heats of reaction and the entropies of reaction. Tai et al.<sup>4</sup> carried out a very extensive study of nylon-6 polymerization in sealed tubes under isothermal condition (230 to 280 °C) and *initial* water concentrations (0.42-1.18 mol/kg). They measured the concentrations of aminocaproic acid by high-pressure liquid chromatography, of  $-NH_2$  and  $-COOH$  end groups by titration and of the cyclic dimer by gas chromatography. They also carried out the numerical integration of the mass balance equations using Reimschuessel's kinetic and equilibrium constants. Good agreement was found between the calculated and experimental values for the caprolactam and the end-group concentrations, but there were large discrepancies in the concentrations of aminocaproic acid and the rates. Hence, they retained the general scheme of Reimschussel et al., but obtained an improved set of kinetic and equilibrium constants using nonlinear regression. The study of Tai et al.<sup>5</sup> shows that the rate constants depend upon the initial water concentrations to some extent. Average values of the rate constants, useful over a limited though relevant range of initial water concentrations (0.42 -1.18



mol/kg) have been reported. These are given in Table 2. More recently Wajge et al.<sup>8</sup> re-tuned the values of  $E_3^c$  and  $\Delta H_3$  using some industrial data, and provided better values for these two parameters (also given in Table 2).

### Modeling and Simulation:

In recent years, numerical simulation and optimization of chemical reactors in general, and polymerization reactors in particular, have become popular for understanding their behavior and improving their performance. The commercial importance of nylon-6 has stimulated considerable research directed towards the modeling and simulation of its polymerization through the hydrolytic route in different kinds of industrial reactors. These have been reviewed by various groups.<sup>1,2,9,12</sup> One such reactor is a semi-batch one in which  $C_1$  and W vaporize into a vapor space, building up the pressure. The vapors are released after some time, in a manner such that a desired pressure history,  $P(t)$ , is maintained. The modeling of such reactors<sup>8</sup> poses severe problems primarily because of lack of good correlations to model the vaporization of  $C_1$  and W. Indeed, the model equations used earlier<sup>8</sup> (see Tables 4 and 5<sup>8,22-26</sup>) for the activity coefficients of CL and W for this reactor have been postulated in a very empirical manner, following some scarce experimental data of Giory and Hayes.<sup>20,21</sup> The following equation is used.

$$\begin{aligned}\gamma_m &= \beta_{mo} + \frac{\beta_{mf} - \beta_{mo}}{0.95} \times \text{monomer conversion} \\ \gamma_w &= \beta_{wo} + \frac{\beta_{wf} - \beta_{wo}}{0.95} \times \text{monomer conversion}\end{aligned}\tag{7}$$

Table 4. Mass and energy balance equations

$$\frac{d[C_1]}{dt} = -k_1[C_1][W] + k'_1[S_1] - k_3[C_1]\mu_0 + k'_3(\mu_0 - [S_1]) - \frac{R_{vm}}{F} + [C_1] \frac{0.113R_{vm} + 0.018R_{vw}}{F}$$

$$\frac{d[S_1]}{dt} = k_1[C_1][W] - k'_1[S_1] - 2k_2[S_1]\mu_0 + 2k'_2[W](\mu_0 - [S_1]) - k_3[S_1][C_1] + k'_3[S_2] - k_5[S_1][C_2] + k'_5[S_3] + [S_1] \frac{0.113R_{vm} + 0.018R_{vw}}{F}$$

$$\frac{d\mu_0}{dt} = k_1[C_1][W] - k'_1[S_1] - k_2\mu_0^2 + k'_2[W](\mu_0 - \mu_1) + k_4[W][C_2] - k'_4[S_2] + \mu_0 \frac{0.113R_{vm} + 0.018R_{vw}}{F}$$

$$\frac{d\mu_1}{dt} = -k_1[C_1][W] - k'_1[S_1] + k_3[C_1]\mu_0 - k'_3(\mu_0 - [S_1]) + 2k_5[C_2]\mu_0 - 2k'_5(\mu_0 - [S_1] - [S_2]) + 2k_4[W][C_2] - 2k'_4[S_2] + \mu_1 \frac{0.113R_{vm} + 0.018R_{vw}}{F}$$

$$\frac{d\mu_2}{dt} = k_1[C_1][W] - k'_1[S_1] + 2k_2\mu_1^2 + \frac{1}{3}k'_2[W](\mu_1 - \mu_3) + k_3[C_1](\mu_0 + 2\mu_1) + k'_3(\mu_0 - 2\mu_1 + [S_1]) + 4k_5[C_2](\mu_0 + \mu_1) + 4k'_5(\mu_0 - \mu_1 + [S_2]) + 4k_4[W][C_2] - 4k'_4[S_2] + \mu_2 \frac{0.113R_{vm} + 0.018R_{vw}}{F}$$

$$\frac{d[C_2]}{dt} = -k_4[C_2][W] + k'_4[S_2] - k_5[C_2]\mu_0 + k'_5(\mu_0 - [S_1] - [S_2]) + [C_2] \frac{0.113R_{vm} + 0.018R_{vw}}{F}$$

$$\frac{d[W]}{dt} = -k_1[C_1][W] + k'_1[S_1] + k_2\mu_0^2 - k'_2[W](\mu_1 - \mu_0) - k_4[W][C_2] + k'_4[S_2] + [W] \frac{0.113R_{vm} + 0.018R_{vw}}{F} - \frac{R_{vw}}{F}$$

$$\frac{dF}{dt} = -(0.113R_{vm} + 0.018R_{vw})$$

$$\frac{dT}{dt} = \left[ UA(T_j - T) + \left[ \frac{F}{1000} \sum_{i=1}^5 [r_i(-\Delta H_i)] \right] - [R_{vm}\lambda_m(T_r) + R_{vw}\lambda_w(T_r)] - (0.113R_{vm}C_{p,m}^v + 0.018R_{vw}C_{p,w}^v) \right] \times \frac{1}{[C'_{p,mix} + 2.0925 \times 10^{-3}(T - T_r)]F}$$

$$\frac{d[M^v]}{dt} = \frac{R_{vm}}{V_g} - \frac{V_r[M^v]}{V_g([M^v] + [W^v] + [N^v])}$$

$$\frac{d[W^v]}{dt} = \frac{R_{vw}}{V_g} - \frac{V_r[W^v]}{V_g([M^v] + [W^v] + [N^v])}$$

$$\frac{d[N^v]}{dt} = -\frac{V_r[N^v]}{V_g([M^v] + [W^v] + [N^v])}$$

$$\frac{d\zeta_1}{dt} = R_{vm}$$

$$\frac{d\zeta_2}{dt} = R_{vw}$$

$$\frac{d\zeta_3}{dt} = V_r$$

$$\mu_3 = \frac{\mu_2(2\mu_2\mu_0 - \mu_1^2)}{\mu_1\mu_0} \text{ and } [S_3] = [S_2] = [S_1]$$

Table 5: Correlations and equations used<sup>8, 22-26</sup>

Expression for  $V_T$

Stage 1:  $V_T = 0$

$$\text{Stages 2-5: } V_T = R_{vm} + R_{vw} - \frac{V_g}{RT} \left( \frac{dP}{dt} \right) + V_g \frac{[M^v] + [W^v] + [N^v]}{T} \left( \frac{dT}{dt} \right)$$

Rates of vaporization

$$R_{vm} = F(k_{l,m}a)_f ([C_1] - [C_1]_f^*)$$

$$R_{vw} = F(k_{l,w}a)_f ([W] - [W]_f^*) + F(k_{l,w}a)_b ([W] - [W]_b^*)$$

where

$$[C_1]_f^* = \frac{[W] + [C_1]}{\gamma_m P_m^{sat}} [M^v] RT$$

$$[W]_f^* = \frac{[W] + [C_1]}{\gamma_w P_w^{sat}} [W^v] RT$$

$$[W]_b^* = \frac{[C_1](P - \gamma_m P_m^{sat})}{(\gamma_w P_w^{sat} - P)}$$

Pressure

$$P = \{[M^v] + [W^v] + [N^v]\} RT$$

Equation for activity coefficients

$$\text{monomer conversion} = 1.0 - \frac{F[C_1]}{F_0[C_1]_0 - \zeta_1}$$

$$\gamma_m = \beta_{mo} + \frac{\beta_{mf} - \beta_{mo}}{0.95} \times (\text{monomer conversion})$$

$$\gamma_w = \beta_{wo} + \frac{\beta_{wf} - \beta_{wo}}{0.95} \times (\text{monomer conversion})$$

Vapor pressure

$$\ln \left[ \frac{P_m^{sat} (\text{kPa})}{101.3} \right] = 13.0063 - \frac{7024.023}{T(\text{K})} \quad (\text{ref. 22})$$

$$\ln \left[ \frac{P_w^{sat} (\text{kPa})}{101.3} \right] = 11.6703 - \frac{3816.44}{T(\text{K}) - 46.13} \quad (\text{ref. 23})$$

Diffusion coefficients

$$D_w (m^2 h^{-1}) = 3.6 \times 10^{-6}$$

$$D_m (m^2 h^{-1}) = 2.88 \times 10^{-8}$$

*Continued*

*Latent heats of vaporization*

$$T_r = 473.15 \text{ K}$$

$$\lambda_w(T_r) = 34.2559 \text{ kJ mol}^{-1} \text{ (Ref.24)}$$

$$\lambda_m(T_r) = 51.0193 \text{ kJ mol}^{-1} \text{ (Ref.24)}$$

$$C_{p,m}^v = 1.6426 \text{ kJ kg}^{-1} \text{ K}^{-1} \text{ (Ref.24)}$$

$$C_{p,w}^v = 1.9963 \text{ kJ kg}^{-1} \text{ K}^{-1} \text{ (Ref.24)}$$

*Heat transfer coefficient*

$$h_i (\text{kJ h}^{-1} \text{ m}^{-2} \text{ K}^{-1}) = \frac{h_{ref}}{[\eta(\text{Pa s})]^{0.17}}$$

$$U = \frac{1}{\frac{1}{h_i} + \frac{\text{thickness (m)}}{k_{ss}}}$$

*Correlations from Re f. 25 for mixture physical properties (liquid)*

$$C_{p,mix}^l (\text{kJ kg}^{-1} \text{ K}^{-1}) = 2.0925 + 2.0925 \times 10^{-3} [T(\text{K}) - 273.15]$$

$$\rho (\text{kg m}^{-3}) = 1000 \{1.1238 - 0.5663 \times 10^{-3} [T(\text{K}) - 273.15]\}$$

$$k (\text{kJ h}^{-1} \text{ m}^{-1} \text{ K}^{-1}) = 0.7558$$

*Correlations from Ref. 26 for mass transfer coefficients*

$$N_{Re} = \frac{d_s^2 n \rho}{6 \eta (\text{poise})}$$

$$N_{Sc,i} = \frac{360 \eta (\text{poise})}{\rho D_i}$$

$$\Omega_b \equiv \left( \frac{[C_1]}{[C_1] + [W]} \gamma_m P_m^{sat} + \frac{[W]}{[C_1] + [W]} \gamma_w P_w^{sat} \right)$$

(i) Quiescent (q) desorption ( $\Omega_b < P$ )

$$N_{Sh,i,q} = 0.322 N_{Re}^{0.7} N_{Sc,i}^{0.33} \quad i = m \text{ or } w$$

$$N_{Sh,i,q} = \frac{(k_{l,i})_{f,q} D_r}{D_i}$$

$$a_{f,q} = \frac{(\pi / 4) D_r^2}{(F / \rho)}$$

$$(k_{l,m} a)_f = (k_{l,m} a)_{f,q}$$

$$(k_{l,w} a)_f = (k_{l,w} a)_{f,q}$$

$$(k_{l,w} a)_b = 0$$

*Continued*

(ii) Bubbly (b) desorption ( $\Omega_b > P$ )

$$\sigma \equiv \frac{[W] - [W_b]^*}{[W_b]^*}$$

$$\sigma_c \equiv 1.81 N_{Re}^{-0.25}$$

If  $\sigma < \sigma_c$ :

$$(k_{l,w}a)_b (h^{-1}) = 6.77 \times 10^{-6} N_{Re}^{0.5} \sigma^{0.78} \times 3600$$

$$(k_{l,m}a)_f = (k_{l,m}a)_{f,q}$$

$$(k_{l,w}a)_f = (k_{l,w}a)_{f,q}$$

If  $\sigma > \sigma_c$ :

$$(k_{l,w}a)_b (h^{-1}) = 2.45 \times 10^{-6} N_{Re}^{0.93} \sigma^{2.5} \times 3600$$

$$\log_{10} \phi = 522(\sigma - \sigma_c) N_{Re}^{-0.81}$$

$$(k_{l,m}a)_f = (k_{l,m}a)_{f,q} \phi$$

$$(k_{l,w}a)_f = (k_{l,w}a)_{f,q} \phi$$

*Viscosity correlation (neglecting effect of water)*

$$\eta_m (\text{cp}) = 2.7969 \times 10^{-4} \exp[3636.364/T(\text{K})]; \quad \text{for } T > 473.15 \text{ K}$$

$$[\eta] \left( \frac{100 \text{ kg mixture}}{\text{kg polymer}} \right) \equiv \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \equiv \lim_{c \rightarrow 0} \frac{\eta - \eta_m}{\eta_m} \frac{1}{c} = \left[ -\frac{1875.0}{T(\text{K})} + 4.678 \right] \left( \frac{M_n}{5424} \right)^{0.75}$$

$$M_n = 113 \mu_1 / \mu_0$$

$$M_n = 113 \mu_2 / \mu_1$$

$$c(\text{kg polymer} / 100 \text{ kg mixture}) = 11.3 \mu_1$$

For  $c < 21.0/[\eta]$

$$\frac{\eta_{sp}}{c[\eta]} = 1.0 - 0.3102c[\eta] + 0.0575(c[\eta])^2 - 0.525 \times 10^{-2}(c[\eta])^3 + 0.02305 \times 10^{-3}(c[\eta])^4 - 0.3663 \times 10^{-5}(c[\eta])^5$$

For  $c > 21.0/[\eta]$

$$\log_{10} \eta (\text{Poise}) = 5 \log_{10} (C'_s M_w^{0.68}) - 12.3097; \quad \text{for } C'_s M_w^{0.68} > 315 \text{ and } M_w > 5000$$

else

$$\log_{10} \eta (\text{Poise}) = \log_{10} (C'_s M_w) - 3.503$$

$$\text{where } C'_s (\text{g polymer}/\text{cm}^3 \text{ mixture}) = 11.3 \times 10^{-5} \rho \mu_1$$

In Eq. 7,  $\beta_{mo}$ ,  $\beta_{mf}$ ,  $\beta_{wo}$ , and  $\beta_{wf}$  are curve-fit parameters, which have been tuned<sup>8</sup> to explain available industrial data. The objective of the present study is to explore if experimental data on both the vapor phase and the liquid phase concentrations can be obtained continuously as a function of time, and better correlations for the rate of evaporation can be developed. Indeed, use of the correlation in Eq. 7, with values tuned on data on the industrial reactor, fails miserably for the data on the laboratory-scale reactor, and emphasizes the need for more fundamental correlations. Two recent papers<sup>27,28</sup> have proposed the POLYNRTL correlation for the activity coefficients,  $\gamma_i(x_i, T)$ , and need to be explored.

## CHAPTER 4

### EXPERIMENTAL RESULTS AND DISCUSSION

In this study, three polymerization runs are carried out with initial water concentrations of 3.45 % (by mass), 2.52 %, and 4.43 %, respectively. During the polymerization, the values of the temperature and the pressure are noted down *manually*. The near-isothermal temperature (245 °C) and the pressure histories are maintained similar to that in the industrial reactor.<sup>8</sup> The temperature of the reaction mass increases from 21 °C to 245 °C in about 38 min and then remains almost constant. Figs. 4-7 show the experimental results for  $[W]_0 = 3.45$  %. The experimental temperature and pressure histories (there is some unintended leakage of vapor even in the first stage) in Figs. 4 and 5 are fitted using empirical equations. These are then used in the model equations (with the values of the parameters the same as obtained for the industrial reactor<sup>8</sup>) to generate the 'simulated' results in Figs. 6 and 7.

Fig. 6 shows the monomer conversion obtained using two different methods (gravimetry and GC) as a function of time for  $[W]_0 = 3.45$  %. It is observed that the two experimental techniques give superposable results over the entire time period. It is also seen that the experimental results match the simulated ones quite well. Fig. 7 shows the experimental values of DP using two methods of end group (amide and acid) analysis, as a function of time. Again, the two techniques give superposable results. However, there is considerable mismatch between the experimental results and the simulated (model) values. This is probably because the correlations for the activity coefficients (Eq. 7),

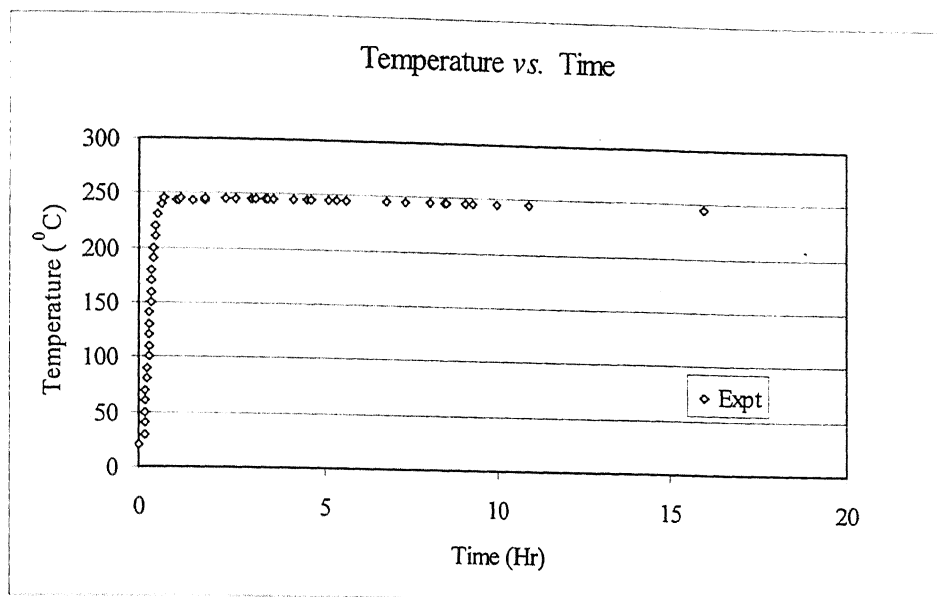


Fig. 4. Experimental temperature history for  $[\text{W}]_0 = 3.45 \%$

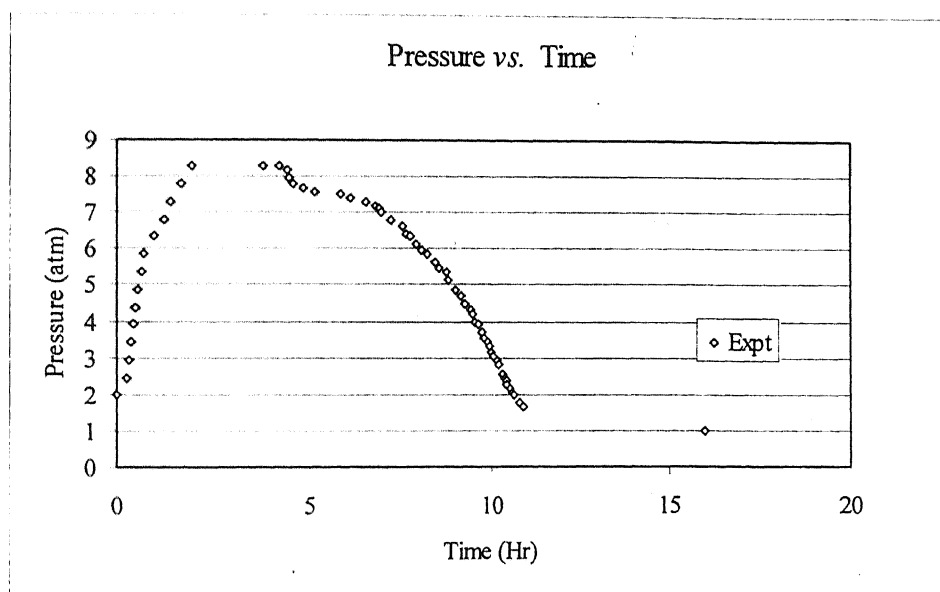


Fig. 5. Experimental pressure history for  $[\text{W}]_0 = 3.45 \%$



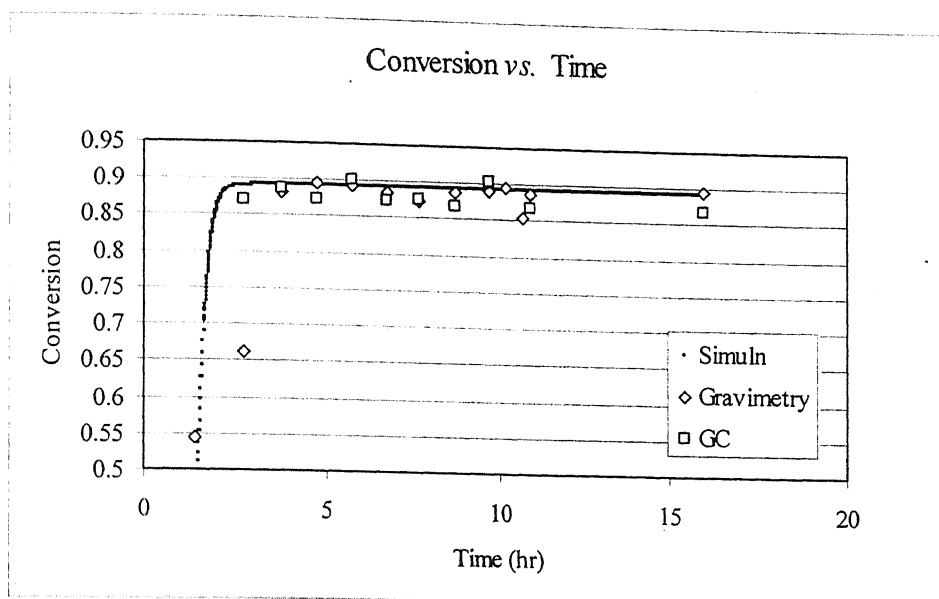


Fig. 6. Variation of the monomer conversion with time for  $[W]_0 = 3.45 \%$

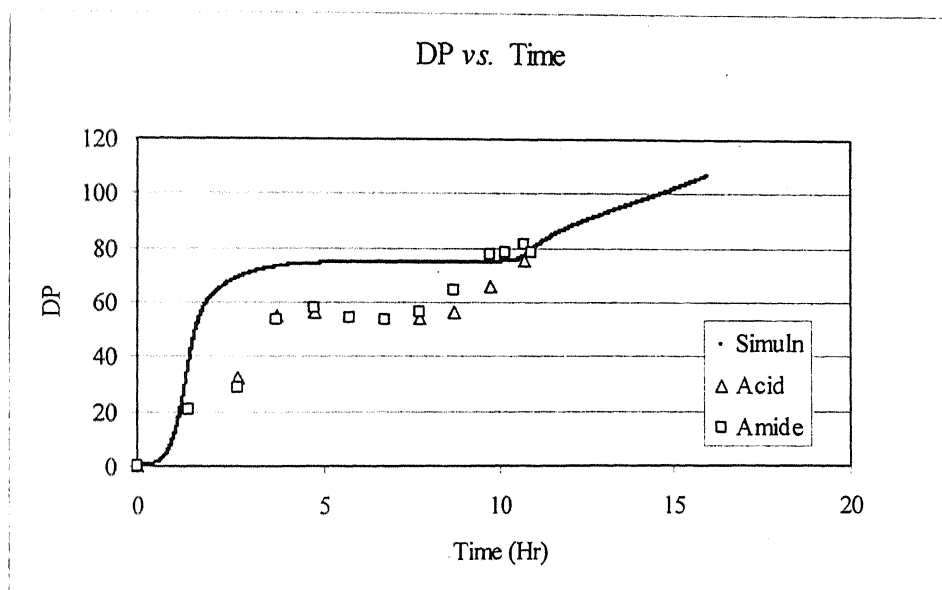


Fig. 7. Variation of the degree of polymerization of the polymer with time for  $[W]_0 = 3.45 \%$

developed using industrial data with extremely empirical equations, may not apply to the much smaller laboratory-scale reactor.

Figs. 8-15 show the experimental results for  $[W]_0 = 2.52\%$  and  $[W]_0 = 4.43\%$ . As in the previous experiment, there is some unintended leakage of vapor in these cases during the first stage.

Figs. 10 and 14 show the monomer conversion obtained using two different methods (gravimetry and GC) as a function of time for  $[W]_0 = 2.52\%$  and  $[W]_0 = 4.43\%$ , respectively. It is observed that the two experimental techniques again give results that are superposable over most of the time period. It may be added that in the beginning there is a considerable amount of flashing of the liquid sample as it exits the reactor. This needs to be accounted for.

Figs. 11 and 15 show the experimental values of DP using two methods of end group (amide and acid) analysis, as a function of time. A considerable amount of mismatch between the experimental results predicted by the two techniques is observed in both the cases. The values predicted by the acid group are found to be lower than those obtained using the amide group concentrations. This could be because of chain scission<sup>29-31</sup> at the high temperatures used ( $150\text{ }^{\circ}\text{C}$ ) during the dissolution of the sample in benzyl alcohol (for the analysis of the acid groups). In addition, chain scission also takes place due to the presence of small amounts of acids (benzoic acid, etc.) in the solvent (benzyl alcohol) used. The values obtain by the amide group analysis are, therefore, presumed to be correct, since polymer degradation is unlikely in this case.

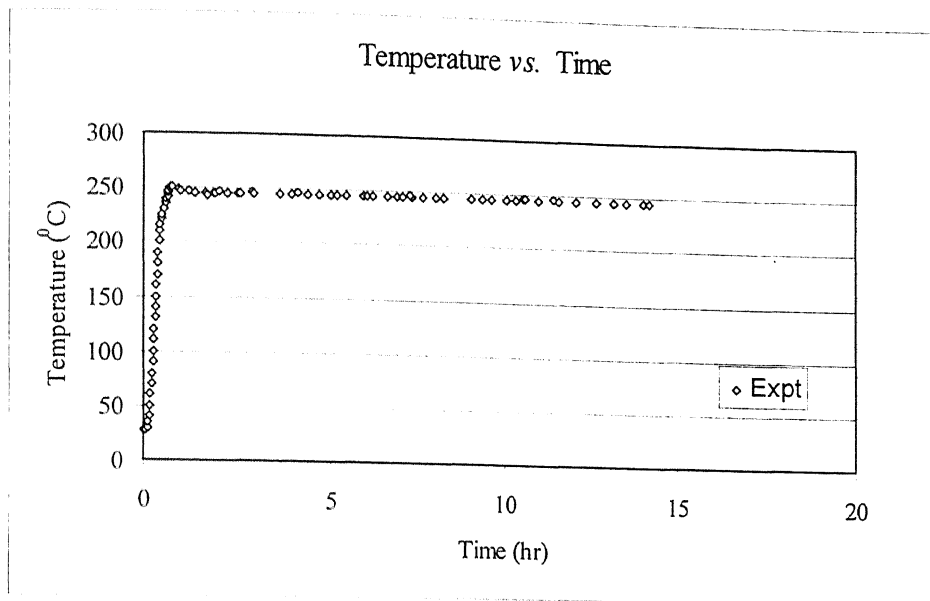


Fig. 8. Experimental temperature history for  $[W]_0 = 2.52 \%$

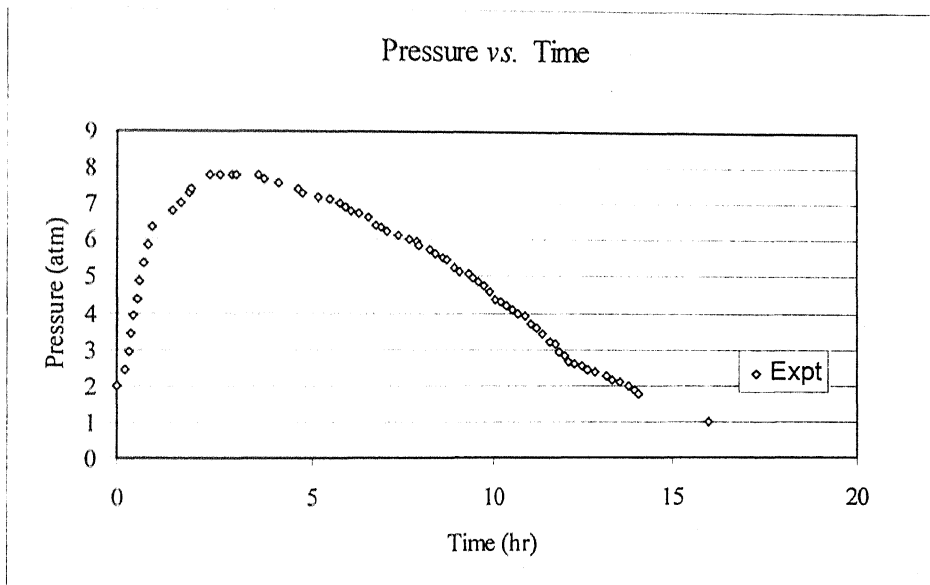


Fig. 9. Experimental pressure history for  $[W]_0 = 2.52 \%$

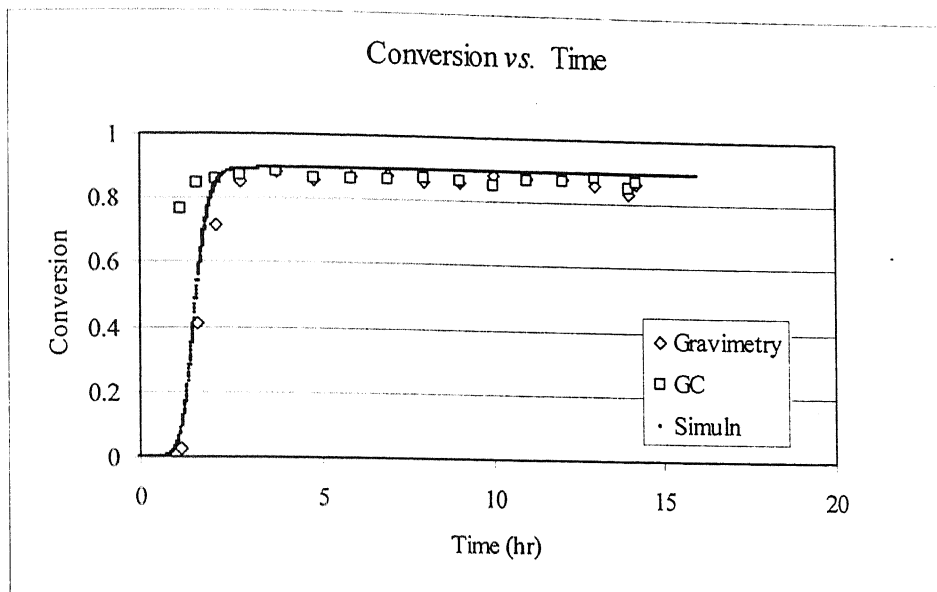


Fig. 10. Variation of the monomer conversion with time for  $[W]_0 = 2.52 \%$

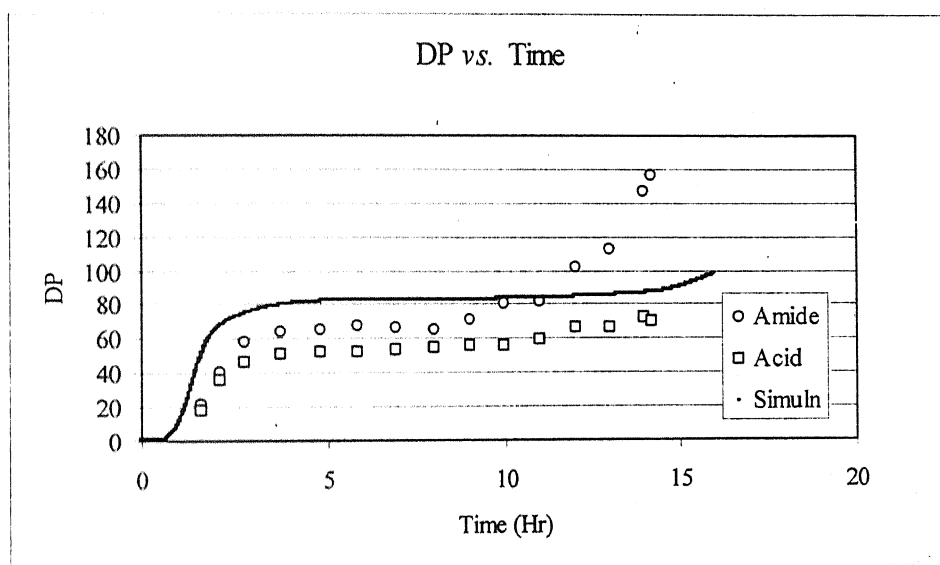


Fig. 11. Variation of the degree of polymerization of the polymer with time for  $[W]_0 = 2.52 \%$

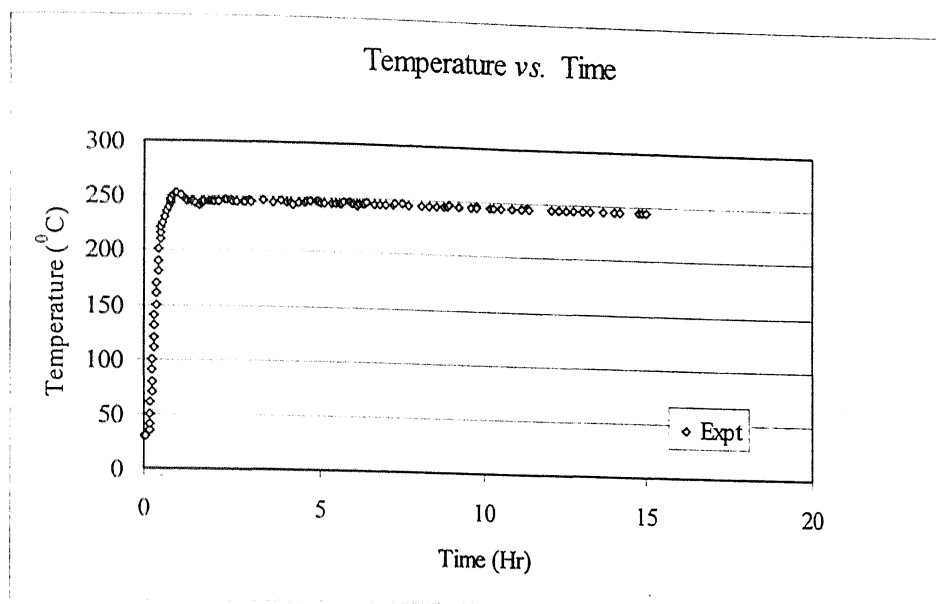


Fig. 12. Experimental temperature history for  $[W]_0 = 4.43 \%$

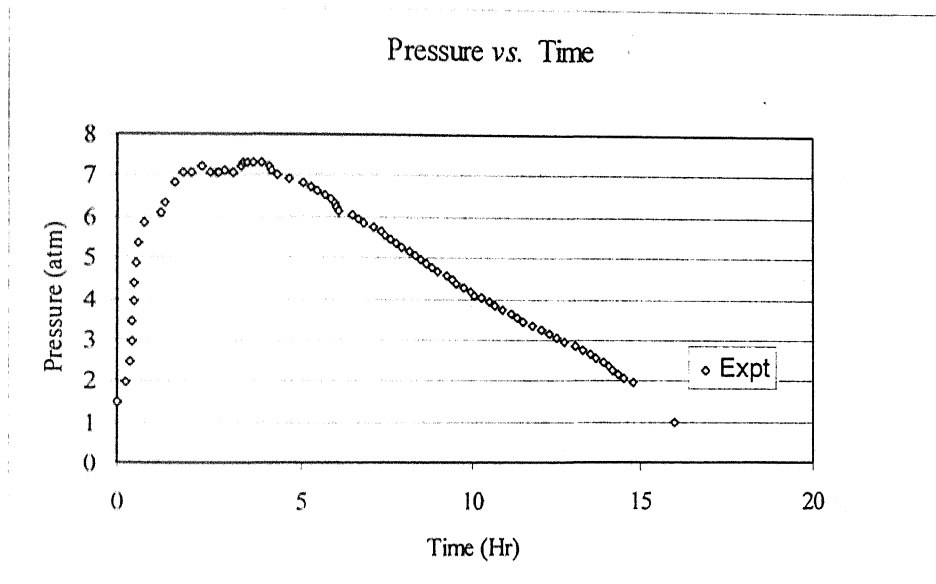


Fig. 13. Experimental pressure history for  $[W]_0 = 4.43 \%$

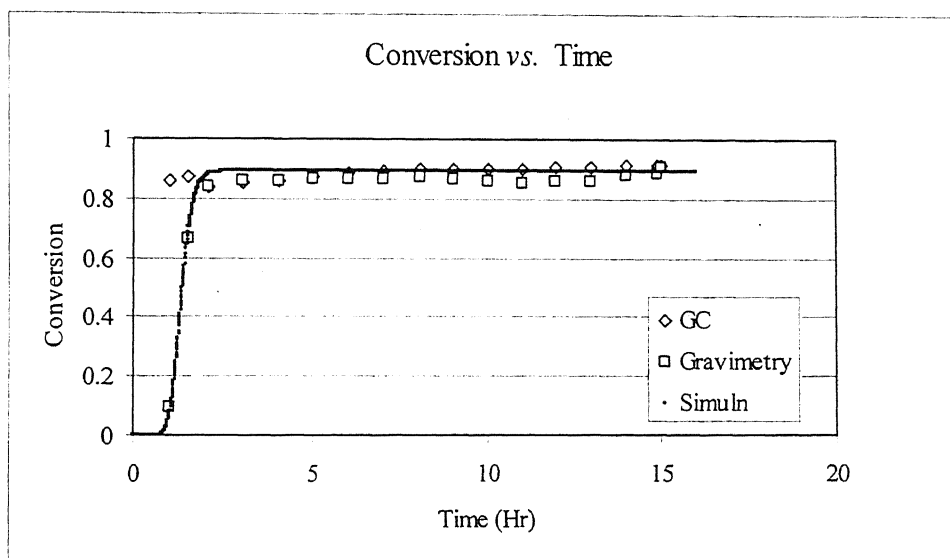


Fig. 14. Variation of the monomer conversion with time for  $[W]_0 = 4.43 \%$

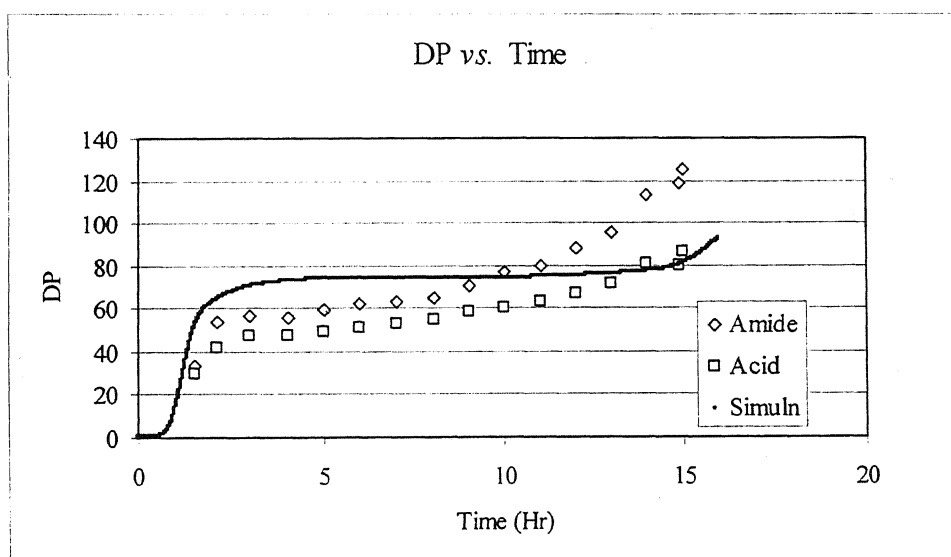


Fig. 15. Variation of the degree of polymerization of the polymer with time for  $[W]_0 = 4.43 \%$

## CHAPTER 5

### CONCLUSIONS

An experimental set-up to study the hydrolytic step growth polymerization of  $\epsilon$ -caprolactam to produce nylon-6 in a semi-batch reactor has been made. A series of experiments under different initial water concentrations have been carried out. The polymerization is carried out under pressure and temperature histories that are similar to those used in industry. The values of the monomer conversions obtained by the two different techniques (gravimetry and GC) superpose, and also match with simulated values (using parameters tuned on an industrial reactor). The degree of polymerization is also obtained using two different techniques (acid and amide end-group analysis). However, there is a considerable mismatch between the values obtained using these two methods. This is possibly because of chain-scission due to the high temperatures used in the preparation of the polymer solution for analysis, as well as due to the presence of acids (benzoic acid, etc.) in the benzyl alcohol used for dissolving the sample for use in the analysis of the acid end-groups. The simulation results for DP do not match with the experimental values (while the monomer conversion, does), and indicates that DP is much more sensitive to the model parameters than the monomer conversion. These experimental results can be used to obtain better estimates of the model parameters. The present set-up needs to be modified, using an on-line gas chromatograph with a heating sampling valve (to measure the concentration of the gas), as well as using virtual instrumentation and control (so that data logging and control of temperature and pressure can be done automatically).

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## APPENDIX A

### Some Sample Calculation

**Calculation (sample 2 of  $[W]_0 = 2.52\%$ ):**

**Conversion (gravimetry):**

Weight of sample before water extraction: 1.4113 gm

Weight of the filter paper used: 1.0974 gm

Weight of the sample and filter paper after extraction and drying: 1.6743 gm

$$\begin{aligned}\text{Conversion} &= \frac{\text{Weight of the sample after extraction and drying}}{\text{Weight of the sample before extraction and drying}} \\ &= \frac{(1.6743 - 1.0974)}{1.4113} \\ &= 0.4087\end{aligned}$$

**Conversion (gas chromatography; volume of liquid introduced = 0.5  $\mu\text{L}$ ):**

Weight of the *pure* caprolactam in 20 ml of water solution (for calibration) : 0.18 gm

Area under the peak of the pure caprolactam sample: 72.287 mV-sec

Weight of the solid sample in 20 ml of water (to prepare extract): 0.5 gm

Area under the peak of extract: 31.241 mV-sec

$$\begin{aligned}\text{Concentration of caprolactam in the polymer sample} &= \frac{0.18 \times 31.241}{72.287} \\ &= 0.0778 \text{ gm}\end{aligned}$$

$$\text{Conversion} = \frac{0.5 - 0.0778}{0.5} = 0.844$$

**Standardization of the solutions:**

KOH dissolved in 100 ml of water: 0.1508 gm

Molecular weight of KOH: 56.11

HCl dissolved in 300 ml of distilled water: 5 ml

KOH dissolved in 100 ml of glycol: 0.1451 gm

Aqueous KOH solution is used to determine the normality of the aqueous acid solution and then this solution is used to find out the normality of the glycol solution.

$$\text{Normality} = \frac{\left( \frac{\text{Weight of solute}}{\text{Molecular weight} \times \text{Valency}} \right)}{\text{volume of the solution in Liter}}$$

$$N_{\text{KOH-W}} = \frac{\left( \frac{0.1508}{56.11} \right)}{0.1}$$
$$= 0.026875$$

$$N_{\text{HCl-W}} V_{\text{HCl-W}} = N_{\text{KOH-W}} V_{\text{KOH-W}}$$

$$11.15 \times N_{\text{HCl-W}} = 10 \times 0.026875$$

$$N_{\text{HCl-W}} = 0.024103$$

Find out  $N_{\text{KOH-Glycol}}$  by titration

$$N_{\text{KOH-Glycol}} V_{\text{KOH-Glycol}} = N_{\text{HCl-W}} V_{\text{HCl-W}}$$

$$N_{\text{KOH-Glycol}} \times 9.3 = 10 \times 0.0223142$$

$$N_{\text{KOH-Glycol}} = 0.025917$$

By direct methods:

$$N_{\text{KOH-Glycol}} = \frac{\left( \frac{0.1451}{56.11} \right)}{0.1}$$
$$= 0.02585$$

**Degree of polymerization:**

**Amide group:**

Sample 2 = 0.2390 gm

Blank titre reading = 0.255 ml

Titre volume = 4.4 ml

$$\text{True titre volume} = (4.4 - 0.255)$$

$$= 4.145 \text{ ml}$$

$$\text{Molecular weight of the monomer} = 113$$

$$M_n = \frac{(\text{sample weight} \times 1000)}{(\text{titer, ml} \times \text{normality})} ; \text{ where } M_0 \text{ is the molecular weight of a repeat unit}$$

$$M_n = \frac{(0.2390 \times 1000)}{(4.145 \times 0.024103)}$$

$$= 2392.222$$

$$DP = x_n = \frac{2392.222}{113} = 21.17$$

**Acid group:**

$$\text{Sample 2} = 0.2621 \text{ gm}$$

$$\text{Blank titre reading} = 0.7 \text{ ml}$$

$$\text{Titre volume} = 5.6 \text{ ml}$$

$$\text{True titre volume} = (5.6 - 0.7)$$

$$= 4.9 \text{ ml}$$

$$\text{Molecular weight of the monomer} = 113$$

$$M_n = \frac{(0.2621 \times 1000)}{(4.9 \times 0.02585)}$$

$$= 2069.23$$

$$DP = x_n = \frac{2069.23}{113} = 18.31$$

## APPENDIX B

### Some Results for the Analysis of Gaseous Samples

#### Gas analysis:

Volume of the gas samples taken for GC: 0.5 ml

**Table B –1 Experimental data on caprolactam concentration in gas phase with respect to time**

| [W] <sub>0</sub> = 3.45% |             |                                  |
|--------------------------|-------------|----------------------------------|
| Time (Hr)                | Area (mV-s) | Conc. of C <sub>1</sub> (gm/lit) |
| 0.833333                 | 22.738      | 2.83E-03                         |
| 2.083333                 | 103.809     | 1.29E-02                         |
| 2.75                     | 130.149     | 1.62E-02                         |
| 4                        | 128.76      | 1.60E-02                         |
| 5                        | 131.376     | 1.63E-02                         |
| 5.25                     | 132.069     | 1.64E-02                         |

#### Calculation:

It has been assumed here that the density of the liquid sample is 1000 times of that the gas.

Weight of the pure caprolactam in 20 ml of water: 0.18 gm

Volume of the liquid sample analysed = 0.5  $\mu$ l

Volume of the gas sample: 0.5 ml

Volume of the 1  $\mu$ l of liquid is equivalent to 1 ml of gas

$$0.5 \text{ ml of the liquid sample has } = \frac{0.18}{20 \times 10^3} \times 0.5 = 4.5 \times 10^{-6} \text{ gm of CL}$$

Area corresponding to the above caprolactam concentration: 72.287 mV-sec

Area of the 0.5 ml gas sample: 22.738 mV-sec

$$\text{Concentration of caprolactam in 0.5 ml gas sample} = \frac{4.5 \times 10^{-6} \times 22.738}{72.287}$$

$$= 1.41548 \times 10^{-6} \text{ gm}$$

$$\text{Concentration of caprolactam in the gas sample} = \frac{1.41548 \times 10^{-6}}{0.5 \times 10^{-3}} = 2.83096 \times 10^{-3} \frac{\text{gm}}{\text{lit}}$$

Some results are shown in fig. B-1

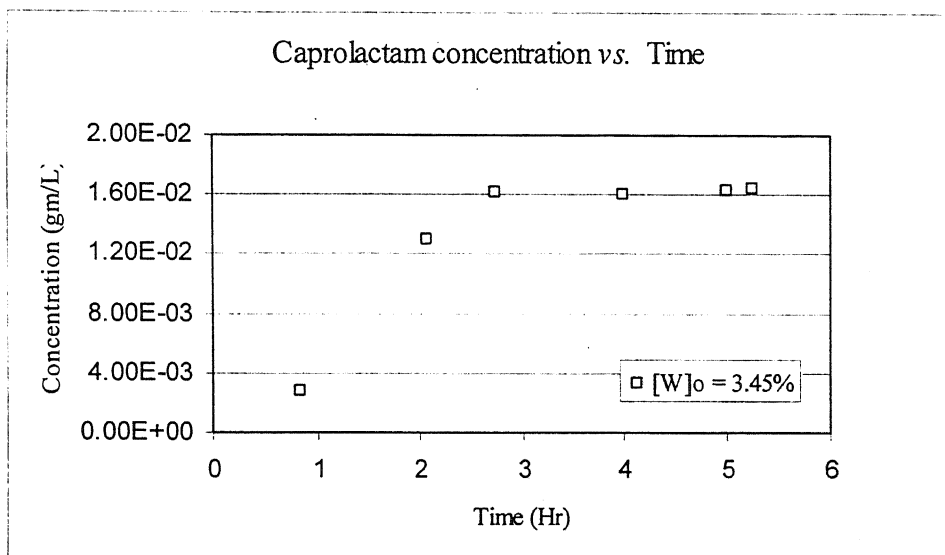


Fig B-1. Variation of the caprolactam concentration in the vapor phase

## APPENDIX C

### Experimental temperature history

**Table C –1 Experimental data on temperature with respect to time**

| $[W]_0 = 3.45\%$ |                                    | $[W]_0 = 2.52 \%$ |                                    | $[W]_0 = 4.43\%$ |                                    |
|------------------|------------------------------------|-------------------|------------------------------------|------------------|------------------------------------|
| Time (Hr)        | Temperature ( $^{\circ}\text{C}$ ) | Time (Hr)         | Temperature ( $^{\circ}\text{C}$ ) | Time (Hr)        | Temperature ( $^{\circ}\text{C}$ ) |
| 0.00             | 21                                 | 0.00              | 27                                 | 0.00             | 29                                 |
| 0.14             | 30                                 | 0.07              | 28                                 | 0.05             | 30                                 |
| 0.15             | 40                                 | 0.11              | 29                                 | 0.15             | 35                                 |
| 0.17             | 50                                 | 0.12              | 30                                 | 0.16             | 40                                 |
| 0.18             | 60                                 | 0.13              | 35                                 | 0.18             | 50                                 |
| 0.19             | 70                                 | 0.15              | 40                                 | 0.18             | 60                                 |
| 0.22             | 80                                 | 0.16              | 50                                 | 0.22             | 70                                 |
| 0.23             | 90                                 | 0.18              | 60                                 | 0.23             | 80                                 |
| 0.25             | 100                                | 0.20              | 70                                 | 0.24             | 90                                 |
| 0.26             | 110                                | 0.21              | 80                                 | 0.26             | 100                                |
| 0.27             | 120                                | 0.24              | 90                                 | 0.27             | 110                                |
| 0.28             | 130                                | 0.26              | 100                                | 0.29             | 120                                |
| 0.30             | 140                                | 0.27              | 110                                | 0.30             | 130                                |
| 0.31             | 150                                | 0.28              | 120                                | 0.31             | 140                                |
| 0.33             | 160                                | 0.30              | 130                                | 0.33             | 150                                |
| 0.34             | 170                                | 0.31              | 140                                | 0.34             | 160                                |
| 0.35             | 180                                | 0.33              | 150                                | 0.36             | 170                                |
| 0.37             | 190                                | 0.34              | 160                                | 0.38             | 180                                |
| 0.39             | 200                                | 0.36              | 170                                | 0.39             | 190                                |
| 0.41             | 210                                | 0.37              | 180                                | 0.41             | 200                                |
| 0.45             | 220                                | 0.39              | 190                                | 0.44             | 210                                |
| 0.51             | 230                                | 0.41              | 200                                | 0.46             | 215                                |
| 0.61             | 240                                | 0.44              | 210                                | 0.49             | 220                                |
| 0.64             | 245                                | 0.45              | 215                                | 0.54             | 225                                |
| 0.99             | 243                                | 0.47              | 220                                | 0.59             | 230                                |
| 1.03             | 244                                | 0.51              | 225                                | 0.64             | 235                                |
| 1.12             | 246                                | 0.54              | 230                                | 0.70             | 240                                |
| 1.41             | 243                                | 0.57              | 235                                | 0.74             | 243                                |
| 1.73             | 244                                | 0.61              | 240                                | 0.75             | 245                                |
| 1.75             | 245                                | 0.62              | 242                                | 0.76             | 246                                |
| 2.28             | 245                                | 0.64              | 244                                | 0.77             | 247                                |
| 2.59             | 246                                | 0.65              | 245                                | 0.82             | 250                                |
| 3.02             | 245                                | 0.66              | 246                                | 0.87             | 252                                |
| 3.11             | 245                                | 0.67              | 247                                | 0.90             | 253                                |
| 3.40             | 246                                | 0.68              | 248                                | 1.06             | 250                                |
| 3.46             | 245                                | 0.69              | 249                                | 1.14             | 247                                |



| $[W]_0 = 3.45\%$ |                                    | $[W]_0 = 2.52\%$ |                                    | $[W]_0 = 4.43\%$ |                                    |
|------------------|------------------------------------|------------------|------------------------------------|------------------|------------------------------------|
| Time (Hr)        | Temperature ( $^{\circ}\text{C}$ ) | Time (Hr)        | Temperature ( $^{\circ}\text{C}$ ) | Time (Hr)        | Temperature ( $^{\circ}\text{C}$ ) |
| 3.62             | 245                                | 0.71             | 250                                | 1.17             | 246                                |
| 4.18             | 245                                | 0.77             | 251                                | 1.22             | 245                                |
| 4.54             | 246                                | 0.78             | 250                                | 1.31             | 244                                |
| 4.66             | 245                                | 0.89             | 249                                | 1.35             | 245                                |
| 5.15             | 245                                | 0.94             | 248                                | 1.37             | 244                                |
| 5.35             | 246                                | 0.99             | 247                                | 1.46             | 243                                |
| 5.62             | 245                                | 1.17             | 246                                | 1.56             | 242                                |
| 6.77             | 245                                | 1.33             | 245                                | 1.61             | 243                                |
| 7.31             | 245                                | 1.61             | 244                                | 1.64             | 244                                |
| 8.01             | 245                                | 1.69             | 243                                | 1.67             | 245                                |
| 8.46             | 246                                | 1.81             | 244                                | 1.77             | 245                                |
| 8.55             | 245                                | 1.90             | 245                                | 1.83             | 244                                |
| 9.05             | 245                                | 2.01             | 246                                | 1.84             | 245                                |
| 9.30             | 245                                | 2.21             | 245                                | 1.92             | 244                                |
| 10.02            | 245                                | 2.47             | 244                                | 1.94             | 245                                |
| 10.92            | 245                                | 2.53             | 245                                | 1.97             | 244                                |
| 16.00            | 245                                | 2.84             | 246                                | 2.06             | 245                                |
|                  |                                    | 2.92             | 245                                | 2.23             | 246                                |
|                  |                                    | 3.59             | 245                                | 2.31             | 247                                |
|                  |                                    | 3.96             | 245                                | 2.39             | 246                                |
|                  |                                    | 4.10             | 246                                | 2.48             | 245                                |
|                  |                                    | 4.38             | 245                                | 2.60             | 244                                |
|                  |                                    | 4.68             | 245                                | 2.60             | 245                                |
|                  |                                    | 5.00             | 245                                | 2.75             | 244                                |
|                  |                                    | 5.18             | 245                                | 2.83             | 245                                |
|                  |                                    | 5.47             | 245                                | 2.92             | 246                                |
|                  |                                    | 5.91             | 245                                | 3.01             | 245                                |
|                  |                                    | 6.02             | 244                                | 3.35             | 246                                |
|                  |                                    | 6.18             | 245                                | 3.59             | 245                                |
|                  |                                    | 6.65             | 245                                | 3.88             | 246                                |
|                  |                                    | 6.89             | 245                                | 4.03             | 245                                |
|                  |                                    | 7.04             | 244                                | 4.13             | 244                                |
|                  |                                    | 7.35             | 245                                | 4.19             | 243                                |
|                  |                                    | 7.67             | 245                                | 4.36             | 244                                |
|                  |                                    | 8.01             | 245                                | 4.53             | 245                                |
|                  |                                    | 8.25             | 245                                | 4.62             | 246                                |
|                  |                                    | 9.07             | 245                                | 4.70             | 247                                |
|                  |                                    | 9.37             | 245                                | 4.89             | 246                                |
|                  |                                    | 9.63             | 245                                | 4.91             | 247                                |
|                  |                                    | 10.07            | 244                                | 4.95             | 246                                |
|                  |                                    | 10.37            | 245                                | 5.02             | 245                                |
|                  |                                    | 10.55            | 246                                | 5.12             | 244                                |

| [W] <sub>0</sub> = 3.45% |                  | [W] <sub>0</sub> = 2.52 % |                  | [W] <sub>0</sub> = 4.43% |                  |
|--------------------------|------------------|---------------------------|------------------|--------------------------|------------------|
| Time (Hr)                | Temperature (°C) | Time (Hr)                 | Temperature (°C) | Time (Hr)                | Temperature (°C) |
|                          |                  | 10.62                     | 246              | 5.36                     | 245              |
|                          |                  | 11.02                     | 245              | 5.47                     | 245              |
|                          |                  | 11.40                     | 246              | 5.57                     | 244              |
|                          |                  | 11.59                     | 245              | 5.65                     | 245              |
|                          |                  | 12.08                     | 245              | 5.66                     | 246              |
|                          |                  | 12.67                     | 245              | 5.71                     | 247              |
|                          |                  | 7.29                      | 246              | 5.87                     | 246              |
|                          |                  | 13.17                     | 245              | 5.94                     | 245              |
|                          |                  | 13.54                     | 245              | 6.00                     | 244              |
|                          |                  | 14.03                     | 245              | 6.07                     | 243              |
|                          |                  | 14.18                     | 245              | 6.10                     | 244              |
|                          |                  |                           |                  | 6.11                     | 243              |
|                          |                  |                           |                  | 6.17                     | 244              |
|                          |                  |                           |                  | 6.25                     | 245              |
|                          |                  |                           |                  | 6.33                     | 245              |
|                          |                  |                           |                  | 6.36                     | 246              |
|                          |                  |                           |                  | 6.61                     | 245              |
|                          |                  |                           |                  | 6.77                     | 245              |
|                          |                  |                           |                  | 6.96                     | 244              |
|                          |                  |                           |                  | 7.19                     | 245              |
|                          |                  |                           |                  | 7.25                     | 246              |
|                          |                  |                           |                  | 7.47                     | 246              |
|                          |                  |                           |                  | 7.65                     | 245              |
|                          |                  |                           |                  | 8.07                     | 244              |
|                          |                  |                           |                  | 8.27                     | 245              |
|                          |                  |                           |                  | 8.50                     | 245              |
|                          |                  |                           |                  | 8.76                     | 244              |
|                          |                  |                           |                  | 8.84                     | 245              |
|                          |                  |                           |                  | 8.92                     | 246              |
|                          |                  |                           |                  | 9.22                     | 245              |
|                          |                  |                           |                  | 9.61                     | 245              |
|                          |                  |                           |                  | 9.74                     | 246              |
|                          |                  |                           |                  | 9.79                     | 245              |
|                          |                  |                           |                  | 10.15                    | 245              |
|                          |                  |                           |                  | 10.26                    | 245              |
|                          |                  |                           |                  | 10.50                    | 245              |
|                          |                  |                           |                  | 10.87                    | 245              |
|                          |                  |                           |                  | 11.14                    | 245              |
|                          |                  |                           |                  | 11.34                    | 246              |
|                          |                  |                           |                  | 11.36                    | 245              |
|                          |                  |                           |                  | 12.05                    | 245              |
|                          |                  |                           |                  | 12.29                    | 245              |

| $[W]_0 = 3.45\%$ |                                    | $[W]_0 = 2.52 \%$ |                                    | $[W]_0 = 4.43\%$ |                                    |
|------------------|------------------------------------|-------------------|------------------------------------|------------------|------------------------------------|
| Time (Hr)        | Temperature ( $^{\circ}\text{C}$ ) | Time (Hr)         | Temperature ( $^{\circ}\text{C}$ ) | Time (Hr)        | Temperature ( $^{\circ}\text{C}$ ) |
|                  |                                    |                   |                                    | 12.51            | 245                                |
|                  |                                    |                   |                                    | 12.76            | 245                                |
|                  |                                    |                   |                                    | 13.06            | 245                                |
|                  |                                    |                   |                                    | 13.26            | 245                                |
|                  |                                    |                   |                                    | 13.68            | 245                                |
|                  |                                    |                   |                                    | 14.00            | 244                                |
|                  |                                    |                   |                                    | 14.17            | 245                                |
|                  |                                    |                   |                                    | 14.78            | 245                                |
|                  |                                    |                   |                                    | 14.90            | 244                                |
|                  |                                    |                   |                                    | 15.00            | 245                                |

## APPENDIX D

### Experimental pressure history

**Table D –1 Experimental data on pressure with respect to time**

| $[W]_0 = 3.45\%$ |                | $[W]_0 = 2.52 \%$ |                | $[W]_0 = 4.43\%$ |                |
|------------------|----------------|-------------------|----------------|------------------|----------------|
| Time (Hr)        | Pressure (atm) | Time (Hr)         | Pressure (atm) | Time (Hr)        | Pressure (atm) |
| 0.00             | 1.97           | 0.00              | 1.97           | 0.00             | 1.48           |
| 0.25             | 2.45           | 0.19              | 2.45           | 0.23             | 1.97           |
| 0.31             | 2.94           | 0.29              | 2.94           | 0.32             | 2.45           |
| 0.36             | 3.42           | 0.35              | 3.42           | 0.38             | 2.94           |
| 0.41             | 3.90           | 0.41              | 3.90           | 0.41             | 3.42           |
| 0.49             | 4.39           | 0.50              | 4.39           | 0.44             | 3.90           |
| 0.56             | 4.87           | 0.59              | 4.87           | 0.47             | 4.39           |
| 0.63             | 5.36           | 0.68              | 5.36           | 0.51             | 4.87           |
| 0.68             | 5.84           | 0.77              | 5.84           | 0.57             | 5.36           |
| 0.97             | 6.32           | 0.88              | 6.32           | 0.71             | 5.84           |
| 1.20             | 6.81           | 1.43              | 6.81           | 1.16             | 6.08           |
| 1.38             | 7.29           | 1.61              | 7.00           | 1.30             | 6.32           |
| 1.66             | 7.77           | 1.81              | 7.29           | 1.56             | 6.81           |
| 1.92             | 8.26           | 1.90              | 7.39           | 1.80             | 7.05           |
| 3.78             | 8.26           | 2.36              | 7.77           | 2.02             | 7.05           |
| 4.18             | 8.26           | 2.63              | 7.77           | 2.26             | 7.19           |
| 4.38             | 8.16           | 2.92              | 7.77           | 2.49             | 7.05           |
| 4.46             | 7.97           | 3.04              | 7.77           | 2.65             | 7.05           |
| 4.56             | 7.77           | 3.58              | 7.77           | 2.75             | 7.05           |
| 4.85             | 7.68           | 3.76              | 7.68           | 2.88             | 7.10           |
| 5.16             | 7.58           | 4.10              | 7.58           | 3.13             | 7.05           |
| 5.82             | 7.48           | 4.66              | 7.39           | 3.35             | 7.19           |
| 6.09             | 7.39           | 4.77              | 7.29           | 3.37             | 7.29           |
| 6.50             | 7.29           | 5.18              | 7.19           | 3.49             | 7.29           |
| 6.78             | 7.19           | 5.47              | 7.10           | 3.65             | 7.29           |
| 6.87             | 7.10           | 5.77              | 7.00           | 3.87             | 7.29           |
| 6.95             | 7.00           | 5.91              | 6.90           | 4.09             | 7.19           |
| 7.22             | 6.81           | 6.05              | 6.81           | 4.19             | 7.10           |
| 7.52             | 6.61           | 6.25              | 6.71           | 4.31             | 7.00           |
| 7.63             | 6.42           | 6.51              | 6.61           | 4.64             | 6.90           |
| 7.76             | 6.32           | 6.75              | 6.42           | 5.03             | 6.81           |
| 7.90             | 6.13           | 6.89              | 6.32           | 5.25             | 6.71           |
| 8.04             | 5.94           | 7.06              | 6.23           | 5.44             | 6.61           |
| 8.22             | 5.84           | 7.36              | 6.13           | 5.65             | 6.52           |
| 8.45             | 5.65           | 7.67              | 6.03           | 5.84             | 6.42           |
| 8.55             | 5.45           | 7.89              | 5.94           | 5.94             | 6.32           |

| [W] <sub>0</sub> = 3.45% |                | [W] <sub>0</sub> = 2.52 % |                | [W] <sub>0</sub> = 4.43% |                |
|--------------------------|----------------|---------------------------|----------------|--------------------------|----------------|
| Time (Hr)                | Pressure (atm) | Time (Hr)                 | Pressure (atm) | Time (Hr)                | Pressure (atm) |
| 8.74                     | 5.36           | 7.96                      | 5.84           | 6.01                     | 6.23           |
| 8.80                     | 5.16           | 8.24                      | 5.74           | 6.07                     | 6.13           |
| 9.03                     | 4.87           | 8.42                      | 5.65           | 6.44                     | 6.03           |
| 9.16                     | 4.68           | 8.63                      | 5.55           | 6.61                     | 5.94           |
| 9.30                     | 4.48           | 8.73                      | 5.45           | 6.78                     | 5.84           |
| 9.44                     | 4.29           | 8.91                      | 5.26           | 7.05                     | 5.74           |
| 9.49                     | 4.19           | 9.08                      | 5.16           | 7.26                     | 5.65           |
| 9.57                     | 4.00           | 9.33                      | 5.06           | 7.37                     | 5.55           |
| 9.63                     | 3.90           | 9.46                      | 4.97           | 7.57                     | 5.45           |
| 9.75                     | 3.71           | 9.63                      | 4.87           | 7.72                     | 5.36           |
| 9.82                     | 3.52           | 9.75                      | 4.77           | 7.88                     | 5.26           |
| 9.92                     | 3.42           | 9.93                      | 4.58           | 8.09                     | 5.16           |
| 9.98                     | 3.32           | 10.09                     | 4.39           | 8.28                     | 5.06           |
| 10.02                    | 3.13           | 10.22                     | 4.29           | 8.43                     | 4.97           |
| 10.07                    | 3.03           | 10.37                     | 4.19           | 8.59                     | 4.87           |
| 10.17                    | 2.94           | 10.55                     | 4.10           | 8.76                     | 4.77           |
| 10.24                    | 2.84           | 10.72                     | 4.00           | 8.92                     | 4.68           |
| 10.34                    | 2.55           | 10.90                     | 3.90           | 9.21                     | 4.58           |
| 10.37                    | 2.45           | 11.06                     | 3.71           | 9.40                     | 4.48           |
| 10.45                    | 2.35           | 11.22                     | 3.61           | 9.50                     | 4.39           |
| 10.47                    | 2.26           | 11.40                     | 3.42           | 9.73                     | 4.29           |
| 10.55                    | 2.16           | 11.61                     | 3.23           | 9.93                     | 4.19           |
| 10.58                    | 2.06           | 11.77                     | 3.13           | 10.05                    | 4.10           |
| 10.66                    | 1.97           | 11.83                     | 2.94           | 10.26                    | 4.00           |
| 10.81                    | 1.77           | 12.01                     | 2.84           | 10.49                    | 3.90           |
| 10.92                    | 1.68           | 12.12                     | 2.65           | 10.68                    | 3.81           |
| 16.00                    | 1.00           | 12.28                     | 2.60           | 10.87                    | 3.71           |
|                          |                | 12.48                     | 2.55           | 11.14                    | 3.61           |
|                          |                | 12.64                     | 2.45           | 11.35                    | 3.52           |
|                          |                | 12.86                     | 2.35           | 11.53                    | 3.42           |
|                          |                | 13.13                     | 2.26           | 11.76                    | 3.32           |
|                          |                | 13.29                     | 2.16           | 12.04                    | 3.23           |
|                          |                | 13.53                     | 2.11           | 12.28                    | 3.13           |
|                          |                | 13.77                     | 1.97           | 12.51                    | 3.03           |
|                          |                | 13.93                     | 1.87           | 12.75                    | 2.94           |
|                          |                | 14.03                     | 1.77           | 13.07                    | 2.84           |
|                          |                | 16.00                     | 1.00           | 13.26                    | 2.74           |
|                          |                |                           |                | 13.48                    | 2.65           |
|                          |                |                           |                | 13.67                    | 2.55           |
|                          |                |                           |                | 13.90                    | 2.45           |
|                          |                |                           |                | 14.05                    | 2.35           |
|                          |                |                           |                | 14.19                    | 2.26           |

| $[W]_0 = 3.45\%$ |                | $[W]_0 = 2.52 \%$ |                | $[W]_0 = 4.43\%$ |                |
|------------------|----------------|-------------------|----------------|------------------|----------------|
| Time (Hr)        | Pressure (atm) | Time (Hr)         | Pressure (atm) | Time (Hr)        | Pressure (atm) |
|                  |                |                   |                | 14.36            | 2.16           |
|                  |                |                   |                | 14.51            | 2.06           |
|                  |                |                   |                | 14.78            | 1.97           |
|                  |                |                   |                | 16.00            | 1.00           |

## APPENDIX E

Experimental values of the degree of polymerization and the monomer conversion

**Table E –1 Experimental data on DP and monomer conversion with respect to time**

for  $[W]_0 = 3.45 \%$

| $[W]_0 = 3.45\%$ |         |         |            |        |
|------------------|---------|---------|------------|--------|
| Time (Hr)        | DP      |         | Conversion |        |
|                  | Amide   | Acid    | Gravimetry | GC     |
| 0.0000           | 0.0000  | 0.0000  | 0.0000     | 0.0000 |
| 1.3667           | 20.5596 |         | 0.5439     |        |
| 2.7028           | 28.7110 | 32.2229 | 0.6621     | 0.8711 |
| 3.7361           | 53.6954 | 55.1483 | 0.8817     | 0.8864 |
| 4.7444           | 57.8330 | 56.1615 | 0.8948     | 0.8725 |
| 5.7361           | 53.9717 |         | 0.8937     | 0.8993 |
| 6.7350           | 53.6181 |         | 0.8832     | 0.8738 |
| 7.6797           | 56.3250 | 54.2412 | 0.8736     | 0.8771 |
| 8.7031           | 64.6330 | 56.6998 | 0.8876     | 0.8681 |
| 9.7028           | 77.4600 | 65.7959 | 0.8903     | 0.9046 |
| 10.1683          | 78.1594 |         | 0.8959     |        |
| 10.7019          | 81.1384 | 75.3289 | 0.8529     |        |
| 10.9200          | 78.1300 |         | 0.8870     | 0.8686 |
| 16.0000          |         |         | 0.8938     | 0.8680 |

**Table E –2 Experimental data on DP and monomer conversion for  $[W]_0 = 2.52 \%$** 

| $[W]_0 = 2.52 \%$ |          |         |            |        |
|-------------------|----------|---------|------------|--------|
| Time (Hr)         | DP       |         | Conversion |        |
|                   | Amide    | Acid    | Gravimetry | GC     |
| 1.0833            |          |         | 0.0239     | 0.7644 |
| 1.5631            | 21.1700  | 18.3100 | 0.4087     | 0.8438 |
| 2.0569            | 40.3410  | 35.7457 | 0.7140     | 0.8578 |
| 2.6983            | 57.8670  | 45.8625 | 0.8533     | 0.8680 |
| 3.7011            | 64.1980  | 50.7040 | 0.8845     | 0.8827 |
| 4.7658            | 65.2950  | 51.6430 | 0.8590     | 0.8617 |
| 5.8200            | 67.5260  | 51.5753 | 0.8675     | 0.8622 |
| 6.8611            | 66.1690  | 53.8753 | 0.8776     | 0.8636 |
| 7.9550            | 65.6460  | 54.9800 | 0.8553     | 0.8673 |
| 8.9972            | 70.7730  | 55.4180 | 0.8588     | 0.8634 |
| 9.9894            | 80.4716  | 55.6800 | 0.8814     | 0.8540 |
| 11.0033           | 81.9810  | 59.5300 | 0.8758     | 0.8679 |
| 12.0367           | 102.1680 | 66.2920 | 0.8764     | 0.8683 |
| 13.0139           | 111.9757 | 66.6080 | 0.8579     | 0.8824 |
| 13.9942           | 146.8290 | 72.3570 | 0.8295     | 0.8512 |
| 14.2058           | 156.2646 | 69.5390 | 0.8633     | 0.8704 |



**Table E –3 Experimental data on DP and monomer conversion for  $[W]_0 = 4.43\%$**

| $[W]_0 = 4.43\%$ |          |         |            |        |
|------------------|----------|---------|------------|--------|
| Time (Hr)        | DP       |         | Conversion |        |
|                  | Amide    | Acid    | Gravimetry | GC     |
| 1.0028           |          |         | 0.8560     | 0.0946 |
| 1.5403           | 33.0720  | 29.9437 | 0.8729     | 0.6636 |
| 2.0981           | 53.7266  | 42.0982 | 0.8394     | 0.8362 |
| 3.0000           | 56.3504  | 47.3635 | 0.8510     | 0.8615 |
| 4.0258           | 55.8337  | 47.2805 | 0.8592     | 0.8589 |
| 5.0028           | 59.7899  | 49.0384 | 0.8697     | 0.8664 |
| 6.0000           | 62.4606  | 50.6310 | 0.8845     | 0.8637 |
| 7.0250           | 62.9151  | 53.0179 | 0.8904     | 0.8648 |
| 8.0472           | 64.6028  | 54.6074 | 0.8977     | 0.8731 |
| 9.0336           | 70.6806  | 58.1972 | 0.8973     | 0.8631 |
| 10.0028          | 77.3593  | 60.3851 | 0.9013     | 0.8598 |
| 11.0139          | 79.3506  | 63.1785 | 0.8974     | 0.8523 |
| 12.0117          | 88.0753  | 67.1426 | 0.9034     | 0.8592 |
| 13.0136          | 95.4574  | 71.1811 | 0.9049     | 0.8603 |
| 13.9911          | 112.8157 | 80.9689 | 0.9128     | 0.8774 |
| 14.8900          | 118.8900 | 80.1671 | 0.9095     | 0.8872 |
| 15.0000          | 124.7644 | 86.3435 | 0.9141     | 0.9052 |